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DETERMINATION OF THE SOURCE OF MIGRATING GAS FROM OIL AND GAS WELLS IN THE LLOYDMINSTER AREA USING STABLE ISOTOPE ANALYSES

by

Kathleen Rich

©

A thesis submitted to the Faculty of Graduate Studies and Research
in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE

DEPARTMENT OF EARTH & ATMOSPHERIC SCIENCES

Edmonton, Alberta

FALL 1995

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled Determination of the Source of Migrating Gas from Oil and Gas Wells in the Lloydminster Area using Stable Isotope Analyses by Kathleen Rich in partial fulfillment of the requirements for the degree of Master of Science.

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Date: October 6, 1995

ABSTRACT

Though Western Canada has greatly benefited from the development of its heavy oil and gas reserves, the proliferation of wells has led to the problem of gas migration to surface around many wellbores. The problem is particularly widespread in the Lloydminster region where leakage occurs at rates up to 200 m^3/day, causing serious industrial and public concern. To date, remedial measures have been expensive and relatively unsuccessful, in part, because the problem is not completely understood. The economics and the effectiveness of attempts to control gas migration will be improved once the origin of the gas is identified.

The key to determining the source of migrating gas observed around wellbores is its isotopic composition. Both the migrating and solution gases of the Lloydminster region are predominantly methane (>96 %) with trace components of higher hydrocarbons. Despite the lack of chemical differentiation, the gases possess unique isotopic signatures.

The methane component of the production horizon gases is very depleted in ^{13}C ($\delta^{13}C_1$ (PDB) ≈ -64 ‰), indicative of a bacterial origin. The trace ethane, propane and butane components of the Mannville Group production gases are relatively enriched in ^{13}C ($\delta^{13}C$ (PDB) ≈ -27 ‰, -21 ‰ and -23 ‰, respectively). The partitioning of $^{13}C/^{12}C$ between propane and butane is reversed in comparison to thermogenic gas, indicating that these higher hydrocarbons have been extensively biodegraded. Therefore, the solution gases of the Lloydminster heavy oils are predominantly bacteriogenic in origin and variably mixed with small amounts of biodegraded thermogenic gas.

The majority of the samples of migrating gas from Lloydminster area wells are tagged by ethane with a $\delta^{13}C$ value of -41 ‰. This signature also characterizes the gases of the shallow Upper Cretaceous strata. The isotope data indicate that the problem of gas leakage originates from the White Speckled Shales and perhaps the overlying Lea Park and Belly River Formations. Preliminary remedial efforts focused on these shallow zones have

been successful at reducing and eliminating the leakage.

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1. INTRODUCTION

1.1 Gas Migration

Disrupting the earth's surface by drilling creates the potential for gases and liquids held in the earth to migrate to shallower horizons or all the way to surface. Gas migration is defined here as the leakage of gas toward the surface from outside the wellbore casings of oil and gas wells or from open hole abandonments (Schmitz *et al*., 1993). Two types of leakage are common (Figure 1.1). Both are observed adjacent to producing and abandoned leases (within metres of the wellbore). In wells completed with a surface casing, a vent flow can be detected in the annulus between the production and surface casings (surface casing migration gas) (Schmitz *et al*., 1993; Erno and Schmitz, 1994). Recent Energy Resource Conservation Board (Forbes and Uswak, 1992) and Husky Oil Drilling and Completion Committee (1992) statistics indicate that 5% of the wells in Alberta equipped with this outer casing demonstrate such a pressure buildup on their surface casings. Gas leakage from petroleum or gas wells can also manifest itself outside the outermost casing (either production or surface casing). Such soil migration gas can be obvious to the eye as gas bubbling up through mud or water pools in the vicinity of the well. Though different in surface manifestation, both types of leakage are indications of gas migrating through the subsurface along the disturbed bore of the well.

The problem of gas leakage is especially prevalent in the shallower heavy oil and gas wells around the City of Lloydminster. In the Lloydminster area, there are five basic scenarios where gas migration from wells is apparent (Saskatchewan Energy and Mines, 1995):

(1) Methane leakage occurs around the wellbore of leases following surface casing completion but prior to drilling into deeper strata.

(2) Migrating gas is observed around the wellbore of wells not equipped with

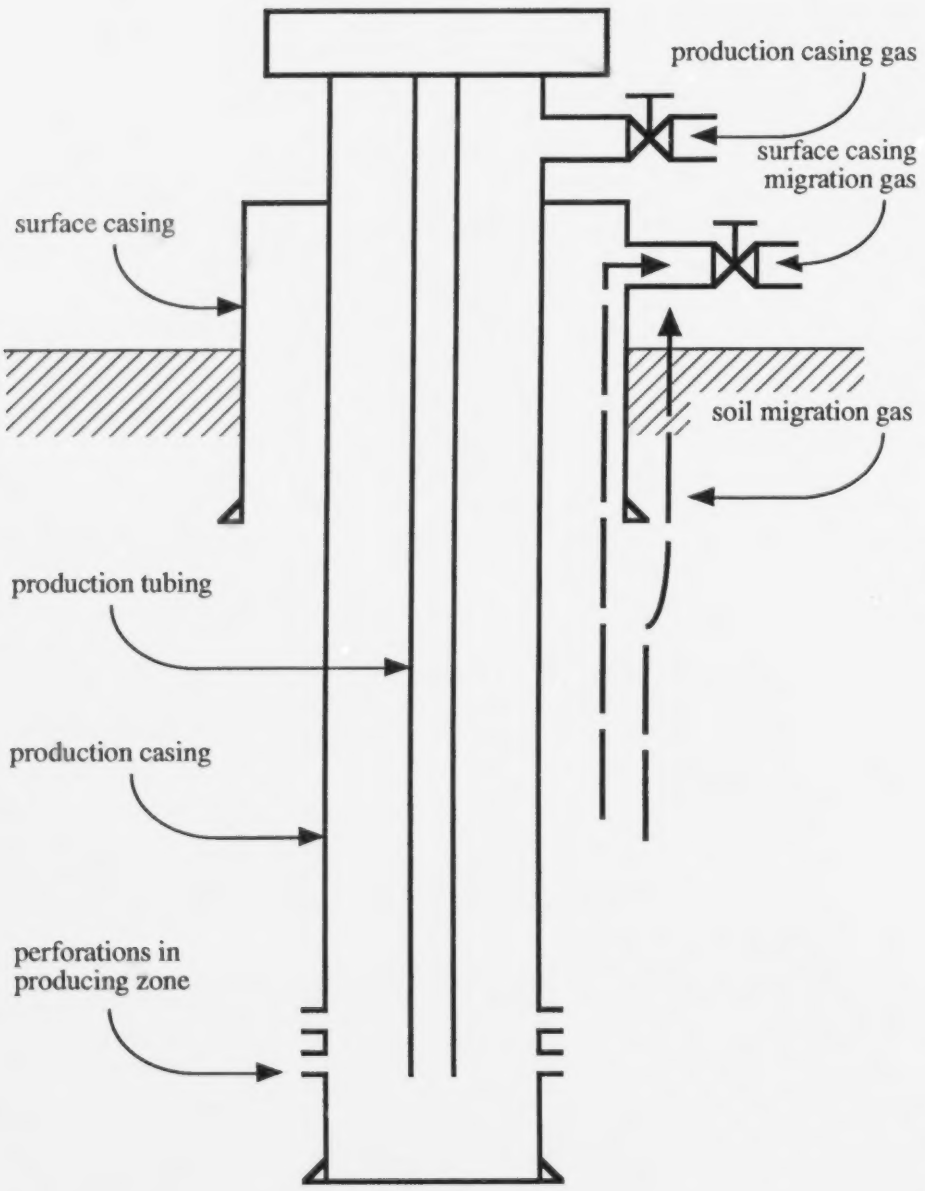


Figure 1.1. Schematic of surface casing and soil migration gas.

surface casings but whose production casings are fully cemented.

(3) Migrating gas from fully cemented wells is also found inside the surface casing and around the wellbore at leases where no leakage was detected prior to drilling the surface casing.

(4) Surface casing gas leaks are observed both in wells whose production casings are cemented in entire length and those whose are not.

(5) Soil migration gas (but not surface casing gas) occurs around wells after cementing the full length of production casing. The problem was not noted prior to drilling deeper than the surface casing depth.

Recognition of the prevalence of natural gas leakage around wellbores in the Lloydminster area of Alberta and Saskatchewan is a reflection of the high shallow well density and extensive agriculture (Jocksch *et al.*, 1993; Schmitz *et al.*, 1993). An eight year study of over 1000 active and abandoned wells in the region conducted by the Petroleum Development Branch of Saskatchewan Energy and Mines revealed that 57% of the examined leases exhibited leakage problems (Saskatchewan Energy and Mines, 1995). The phenomenon was visible in all areas checked by the branch, and all operators experienced the problem. Surface casing vent leakage rates between 0.01 and 200 m^3/day were measured (Schmitz *et al.*, 1993; Erno and Schmitz, 1994); soil migration gas rates varied between 0.01 and 60 m^3/day (Erno and Schmitz, 1994). Less than 10% of the Lloydminster region wells demonstrating surface casing gas migration and less than 15% of those exhibiting soil gas migration did so at rates faster than 1 m^3/day (Jocksch *et al.*, 1993; Schmitz *et al.*, 1993).

Gas leakage in the Lloydminster area was acknowledged in 1979 when farmers complained of soil migration gas damaging crops and operators encountered gas kicks while drilling wells (Saskatchewan Energy and Mines, 1995). The problem of gas migration from wells has received increasing attention in recent years for many reasons

including:

(1) Since its recognition, regulators and industry have become aware of the large number of wells affected and the difficulty in mitigating the leakage.

(2) More and more wells are nearing the end of their economic lives and will soon require abandonment (Schmitz *et al.*, 1993).

(3) The concern of industry and the public regarding the potential environmental effects (groundwater contamination, the release of hydrocarbon vapours into the atmosphere, etc.) is rising (Chafin, 1992; Forbes and Uswak, 1992).

Though the only acknowledged impact of gas leakage is productivity damage to a few tens of metres of land surrounding some wells (Godwin *et al.*, 1990; Jocksch *et al.*, 1993), the possibility of migrating gas contaminating fresh water aquifers is postulated and under investigation (Beckstrom and Boyer, 1991; Finch, 1991; Saskatchewan Energy and Mines, 1995). This is discussed in Appendix 4.

To date, investigations into the migration of gas from leaking wells have centered on identifying problem wells and standardizing test methods. Little is known about the pathways followed by migrating gas from depth toward the surface around wellbores. Plausible migration routes include poorly abandoned wells, inadequately cemented wells, corroded operating wells and natural or induced fractures in the production horizon (Saskatchewan Research Council, 1995). Special attention has thus been provided to the quality and amount of cement blends used, cement waiting times, surface casing depths and general drilling procedures (Saskatchewan Energy and Mines, 1995). However, cement squeezes and other remedial work exhausted on the producing zones in the Lloydminster region have been case-specific, time consuming, expensive and have had little effect on gas leakage except in rare cases (Jocksch *et al.*, 1993; Schmitz *et al.*, 1993).

Regulatory guidelines state that gas leaks must be eliminated prior to well operation and abandonment (Erno and Schmitz, 1994; Saskatchewan Energy and Mines, 1995). Any amount of gas migration to surface resulting from industry activities is considered too much (Saskatchewan Energy and Mines, 1995), and surface gas leaks are required to be shut off at or near their source (Energy Resource Conservation Board, 1990). Further, verification of repair is obligatory. Currently, abandonment of leases which have reached the end of their productive lives is being put off due to the lack of technically reliable and economically feasible methods of gas leakage elimination.

1.2 Objectives

Recently, the near-surface accumulation of natural gas in soils has become an environmental concern to the oil and gas industry. Thus far, efforts to eliminate gas migration associated with wells have been well-specific, costly and of limited success. This is simply a reflection of the current lack of understanding of the problem. The source of the gas and its migration path to surface are not clear. To improve the effectiveness of remedial measures a shift from identifying and quantifying the problem to assessing its mechanisms (origin and pathway) is needed. The objective of this study is to determine the source(s) of migrating gas from leaking wells in the Lloydminster area.

1.3 Distinguishing Gases

Differentiation of the migrating gas observed around Lloydminster area wellbores from other gases is essential to determining the source of gas leaks. Therefore, a procedure or tool which enables a distinction to be made between various gases is necessary. The use of bulk composition seems most obvious.

Natural gases are divided into primary and secondary types (Table 1.1). Primary gases, those generated from a single source of organic material, include diagenetic,

Table 1.1. Natural gas types (modified after Whiticar, 1994).

Type	Comments
Primary	
Diagenetic	Low temperature
Bacteriogenic:	
CO_2 reduction	Marine
Methyl-type fermentation	Freshwater
Thermogenic	Associated and not associated with oil
Mature	Hydrocarbon window
Late mature	Condensate
Geothermal or hydrothermal	
Crystalline	
Juvenile or abiogenic	Mantle
Secondary	
Mixed gases	
Altered or biodegraded	
Weathered or water washed	
Migration fractionation	

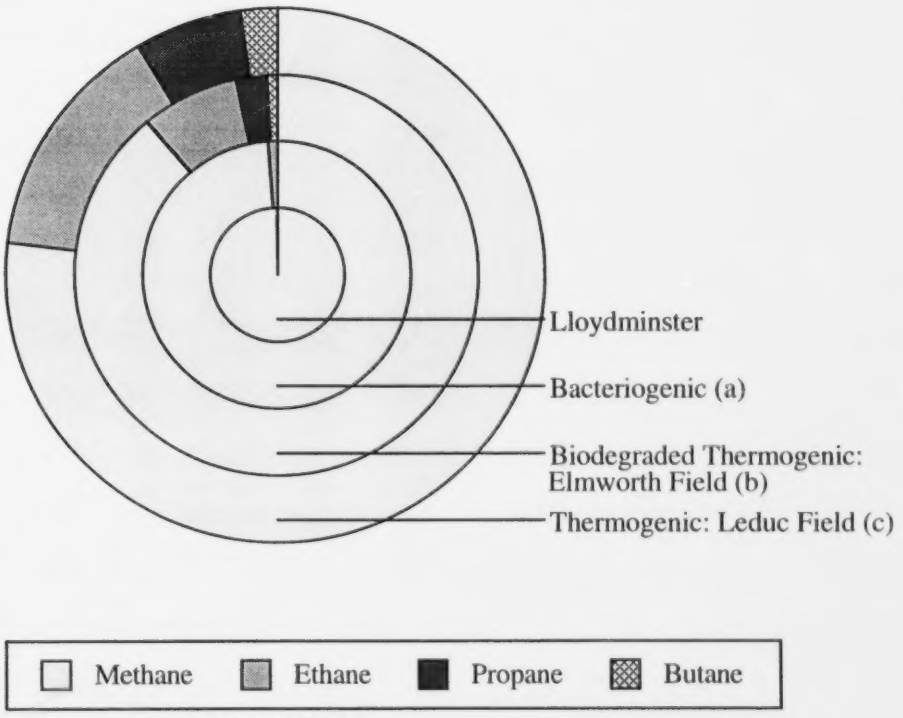
bacterial, thermogenic, geothermal/hydrothermal, crystalline and juvenile gases (Whiticar, 1994). Natural gases are, however, principally produced from the alteration of organic matter by either biologic or thermocatalytic processes (Schoell, 1980; Stahl *et al.*, 1981). In the early stages of diagenesis, bacteria produce gases which are predominantly methane (Figure 1.2). Traces of higher hydrocarbons (C_{2+}) have, however, been detected in these bacteriogenic gases (Rice, 1975; Whiticar, 1994), but the amount of C_{2+} (generally ethane) produced by bacteria is usually less than 1 % of the methane generated in the same environment (Whiticar, 1994). Increasing thermal maturation of organic source material continues to generate methane but also yields ethane, propane and butane (Schoell, 1980). As methane is produced during all stages of the maturation of organic matter, thermogenic gas is also dominantly methane, but it contains significant amounts of C_{2+} (Figure 1.2). A similar distribution of higher hydrocarbons is observed in biodegraded thermogenic gas, but biodegraded gas tends to have less significant C_{2+} fraction (Figure 1.2). Biodegraded thermogenic gas is the residual gas remaining after bacteria have consumed portions of a thermogenic gas reservoir. This secondary natural gas is more enriched in lighter hydrocarbons as bacteria preferentially utilize the higher molecular weight forms (i.e. propane and butane) as organic sources (James and Burns, 1984; James, 1990). Thus, the relative proportions of higher hydrocarbons to methane can be used to differentiate gases of different origins. In general, bacteriogenic gases have ratios of methane to C_{2+} of at least 100 (often more than 1000) (Stahl, 1974; Schoell, 1983); such ratios in thermogenic gases tend to value less than 50 (Bernard *et al.*, 1977). Gases of different origins may, therefore, be chemically distinguishable.

The solution gases associated with the Lloydminster region heavy oil fields, like the migrating gas observed around oil and gas wells in the area, are predominantly methane (>96 %) with trace measures of carbon dioxide and higher hydrocarbons (Table 1.2). Compositionally, the gases are indistinct. Moreover, during migration toward surface, diffusion, sorption and desorption processes are known to alter the composition

Table 1.2. Composition of a typical Lloydminster area production gas.*

Component	Mol % (air free)
N_2	2.55
CO_2	0.62
C_1 (methane)	96.44
C_2 (ethane)	0.34
C_3 (propane)	0.03
iC_4 (iso-butane)	0.01
nC_4 (normal butane)	0.01

* The listed chemistry is that of a Colony horizon sample from Amoco Canada Petroleum's 9-6-55-6 W4M well. This sample's composition was analyzed at Chemex Labs Alberta Incorporated as well as at the University of Alberta.



(a) SOURCE: Whiticar (1994)

(b) SOURCE: James and Burns (1984)

(c) SOURCE: James (1990)

Figure 1.2. Comparison of the composition of Lloydminster area gas and that typical of different gas types.

of natural gas (Stahl *et al*., 1981). In particular, migration tends to increase the methane to C_{2+} ratio (Coleman *et al*., 1977), rendering discrimination between bacteriogenic and migrated thermogenic gas difficult (Grossman *et al*., 1989). It is also likely that phase separation during sampling affects the trace higher hydrocarbon content. Consequently, bulk composition is not a good approach to resolving the source of gas leakage.

Characterization of the migrating gas observed around wellbores can be accomplished using stable isotope analyses. Isotopes are atoms with the same number of protons but different numbers of neutrons. Having the same atomic number, isotopes of a given element behave similarly, but the slight variations in mass cause isotopic fractionation. Fractionation is any process that causes the isotopic composition of different phases to vary. Fractionation is induced by isotope exchange reactions as well as by mass dependent differences in the rates of given chemical, physical and biological processes (Drever, 1988; Faure, 1991).

The stable carbon and hydrogen isotopic compositions of natural gas are known to be an indication of the type and maturity of its source rock (Stahl and Carey, 1975; Stahl, 1977; Deines, 1980; Feux, 1980; Horvitz, 1980; Schoell, 1980; James, 1983; Berner and Faber, 1988; James, 1990; Whiticar, 1994) and its origin (thermal cracking versus bacterial decomposition) (Deines, 1980; Feux, 1980; Schoell, 1980; Stahl *et al*., 1981; Balabane *et al*., 1987; James, 1990). The isotopic ratios are essentially unchanged by migration through the subsurface. Measured changes in the carbon isotopic ratio of migrated methane in natural systems are normally smaller than 1 ppt (Stahl and Carey, 1975; Feux, 1980; Grossman *et al*., 1989; James, 1990). Thus, isotopic studies are a useful geochemical method of fingerprinting gases, and they could be helpful in determining the origin of gas leaks.

Interpretation of the source and maturity relationships of a given reservoired gas relative to another has been executed using methane isotope data alone. However, the isotopic likeness of multiple reservoirs within a section, the mixing of gases from various

sources, biodegradation and secondary thermal alteration of gases and the uncertain nature of migration pathways obscure such correlation (James, 1990). Determination of the isotopic content of the higher hydrocarbons can lessen these correlation uncertainties (Galimov, 1988; Chung *et al*., 1988; James, 1990). Propane and butane isotope signatures have been found especially useful for correlation purposes (James, 1990). The carbon isotope makeup of these higher hydrocarbons seems to near that of their source. The iso-butane carbon isotope composition appears to be principally inherited from its source (James, 1990). The isotopic signature of propane also displays a significant connection to maturity (James, 1990).

The stable isotopes of carbon and hydrogen and their masses, relative abundances and measurement standards are listed in Table 1.3. Isotopic abundances are commonly measured and reported as delta (δ) values which represent the part per thousand (per mil) deviation of the isotopic ratio of a sample from that of a standard. The δ values reported in this text are expressed in terms of the Peedee Formation belemnite (PDB) standard for carbon (Craig, 1957) and Standard Mean Ocean Water (SMOW) for hydrogen (Hagemann *et al*., 1970). The following equation depicts the δ notation:

$$\delta\,^{13}C\,(‰) = \frac{\left(\,{}^{13}C/^{12}C_{sample} - {}^{13}C/^{12}C_{standard}\,\right) \times 1000}{{}^{13}C/^{12}C_{standard}}$$

An analogous expression defines δD. More positive δ values reflect a relative enrichment of the heavier isotope in the sample. Such specimens are isotopically "heavy." "Light" samples have more negative δ values and are relatively depleted in the heavier isotope compared to the standard.

1.4 Methodology

Two groups of gases from the Lloydminster area were gathered and isotopically

Table 1.3. Abundances, masses and primary reference standards of hydrogen and carbon stable isotopes.

Element	Isotope	Mass (amu)[a]	Relative Abundance (%)[b]	Standard
Hydrogen	^{1}H	1.007 825	99.9844	SMOW; Standard Mean Ocean Water; D/H = 155.76×10^{-6} (Hagemann *et al.*, 1970)
	^{2}H (D)	2.014 000	0.0156	
Carbon	^{12}C	12.000 000	98.89	PDB; Peedee Formation Belemnite; $^{13}C/^{12}C = 1123.75 \times 10^{-5}$ (Craig, 1957)
	^{13}C	13.003 355	1.11	

[a] SOURCE: Weast *et al.* (1986)
[b] SOURCE: Kyser (1987)

analyzed. The first was a set of about 120 samples (66 wells) from the producing heavy oil-associated Mannville and Colorado Group strata. These gases were sampled from sound wells (no known problems) with single completions, to assure their being representative of the given horizons. The objectives of this first data set were to evaluate the procedure, to determine repeatability and to create an information library of the various formations. The second set comprised approximately 40 migrating gas samples (20 wells). The "leaking" well samples were obtained both from surface casing vents and from bubbles around the wellhead. The soil migration gas samples were collected within feet of the outer casing of the well. The objectives of this second data set were to characterize the migrating gas associated with leaking wells of the Lloydminster region and to determine any differences between vent flow and soil migration gases.

The three types of gas samples were collected in 2 L Tedlar Teflon™ bags or steel bombs at or near atmospheric pressure. The production and surface casing gases were obtained directly from well vents. The sampled surface casing vents were "blown off" (vented) and had to be shut in prior to gas collection. This pressure buildup took minutes to days depending on the well. The gas bubbles escaping through water and mud pools around the wells were trapped by attaching collection bags to an overturned pail (Figure 1.3). Bulkhead fittings and a valve were added to the base of a 20 L plastic pail. A piece of one inch pipe was strapped to the pail, acting as a guide to hold the pail over the bubbles. The pail was filled with water and tipped upside down over the gas bubbles, and as the soil migration gas was trapped inside, the pail would float upward. When enough gas had collected in the pail, usually one or two days, a hand bulb pump was attached to the valve to fill a Tedlar bag with gas.

The gases were separated into their components with a Hewlett-Packard 5980 gas chromatograph equipped with a Poropak Q-packed glass column kept at 40 °C (Figure 1.4). After sample introduction, the temperature was increased by 20 °C/min up to 150 °C. Methane (C_1) was eluted in 3 minutes, and the carbon dioxide (CO_2) peak appeared

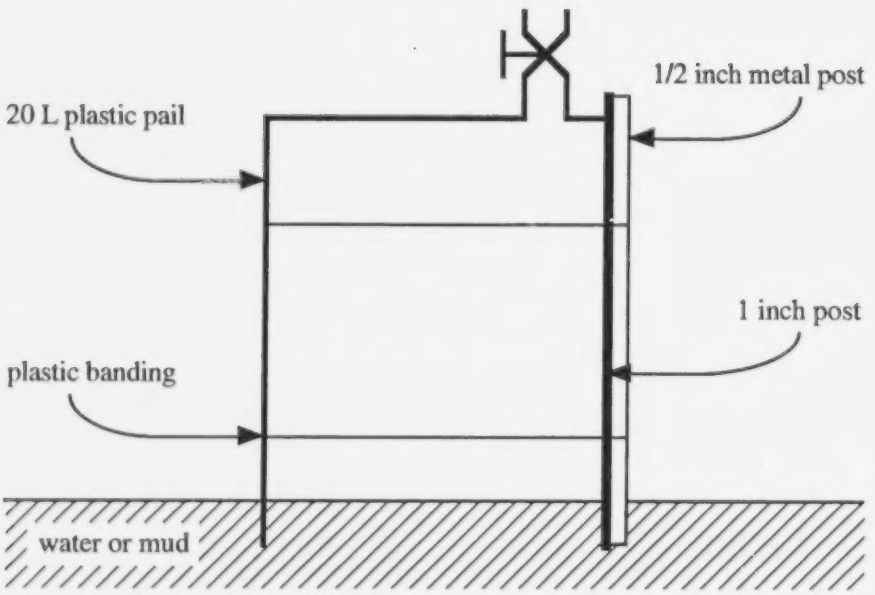


Figure 1.3. Sampler for bubbles in water and mud.

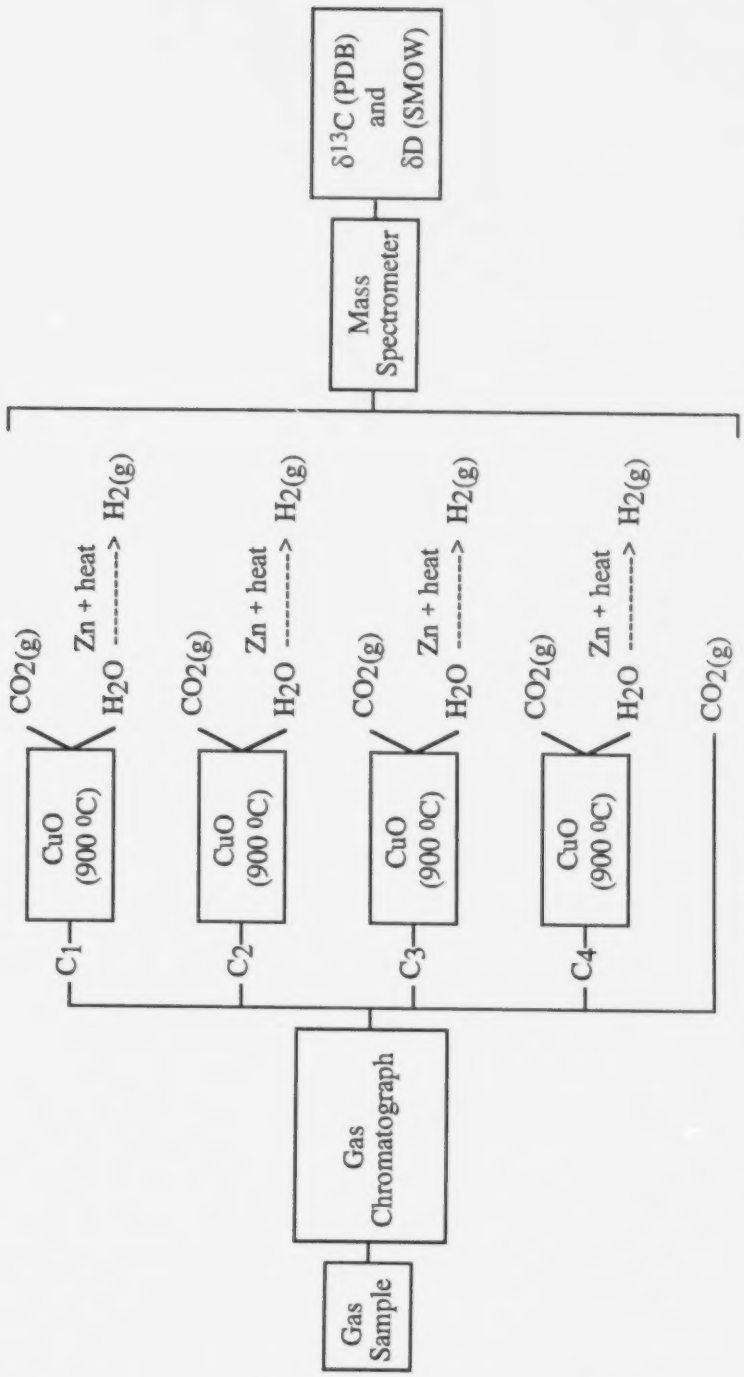


Figure 1.4. Flow chart depicting sample analysis.

3.5 minutes later. Higher hydrocarbons (ethane (C_2), propane (C_3) and butane (C_4)) were well separated in order of increasing molecular mass. The last peak, that of normal-butane, occurred 27.5 minutes into the run. With the exception of carbon dioxide, each eluted gas was routed through individual quartz furnace tubes containing hot (900 °C) CuO. The combustion products, CO_2 and H_2O, were collected in glass coil traps cooled in liquid N_2. The He carrier stream was pumped from the frozen samples. The liquid N_2 baths were replaced by dry ice-ethanol mixtures which retained the water H_2O while the CO_2 thawed and was transferred into collection tubes. The H_2O samples were collected and heated with Zn metal to produce $H_{2(g)}$ (Coleman *et al.*, 1982). This H_2 and CO_2 were isotopically analyzed for their D and ^{13}C content using a Finnigan-MAT™ 252. The pooled residual variance of replicate isotope analyses is summarized in Table 1.4.

1.5 Summary

The Lloydminster heavy oil region is nicknamed the "headache" area in the oil industry due to the prevalence of "leaking" gas wells in the vicinity. It is estimated that natural gas is migrating to surface, through surface casing vents and soils, in half of the wells in the vicinity of the City of Lloydminster. There is concern that the methane may migrate and possibly contaminate surficial aquifers of potable water.

Due to the current lack of understanding of the problem, approaches to controlling the leakage have been case-specific, expensive and of minor success. Little is known about the origin and pathway followed by migrating gas. Determining the source of migrating gas associated with producing and abandoned wells is a key step in solving the problem.

The solution and migrating gases of the region are chemically indistinct, and phase separation during sampling or migration may not be consistent. Therefore, bulk composition is not a useful tool for characterizing gas migrating from Lloydminster area

Table 1.4. Pooled residual variance of replicate isotope analyses.

Analysis	Standard Deviation (‰)
$\delta^{13}C$ (PDB) C_1	2
$\delta^{13}C$ (PDB) C_2	2
$\delta^{13}C$ (PDB) C_3	2
$\delta^{13}C$ (PDB) C_4	1
$\delta^{13}C$ (PDB) CO_2	3
δD (SMOW) C_1	23
δD (SMOW) C_2	35
δD (SMOW) C_3	28
δD (SMOW) C_4	24

wells. The stable isotopes of natural gas are not significantly altered by migration and are known to reflect the type and maturity of the gas. Isotopic analyses are therefore a logical approach to determining the origin of gas leakage.

2. GEOLOGICAL CHARACTERIZATION OF THE LLOYDMINSTER AREA

2.1 Location of the Study Area

The study region, located around the central portion of the Alberta-Saskatchewan border, surrounds the City of Lloydminster (Figure 2.1). The area encompasses Townships 42 through 61 and Ranges 24 W3M to 11 W4M and contains all the major Lloydminster heavy oil fields (Figure 2.2).

Within the outlined Lloydminster region lies the Lindbergh field (Figure 2.2). The Lindbergh area of east-central Alberta comprises the 2880 km^2 held within Townships 52 to 58 and Ranges 3 to 7 W4M. Most of the sampling was restricted to the central portions of the Lindbergh area (Townships 54 to 56, Ranges 4 to 6 W4M) where oil and gas wells are abundant.

The use of the land is dominantly agricultural. Thus, the gently rolling plain is essentially bare of wooded areas. Densely-spaced oil and gas wells, producing from shallow deposits, characterize the region.

2.2 Geological Framework

Approximately 12,000 wells have been drilled in the Lloydminster area of Alberta and Saskatchewan (Smith *et al.*, 1984). The heavy oil fields of the region produce mainly from the Lower Cretaceous Mannville Group (Smith, 1984) which is estimated to contain between 40 and 60 billion barrels (8 - 11 billion m^3) of oil in place (Smith *et al.*, 1984; van Hulten and Smith, 1984). Regionally, the sand-shale cycles comprising the Mannville Group formations strike northwesterly and have a gentle southwesterly dip of 1.9 m/km which is accentuated by their thinning toward the south (White and Shultz, 1977; Putnam, 1983; Smith *et al.*, 1984). The units are relatively undeformed in the Lloydminster region (Putnam, 1983), and the Mannville structure appears to have

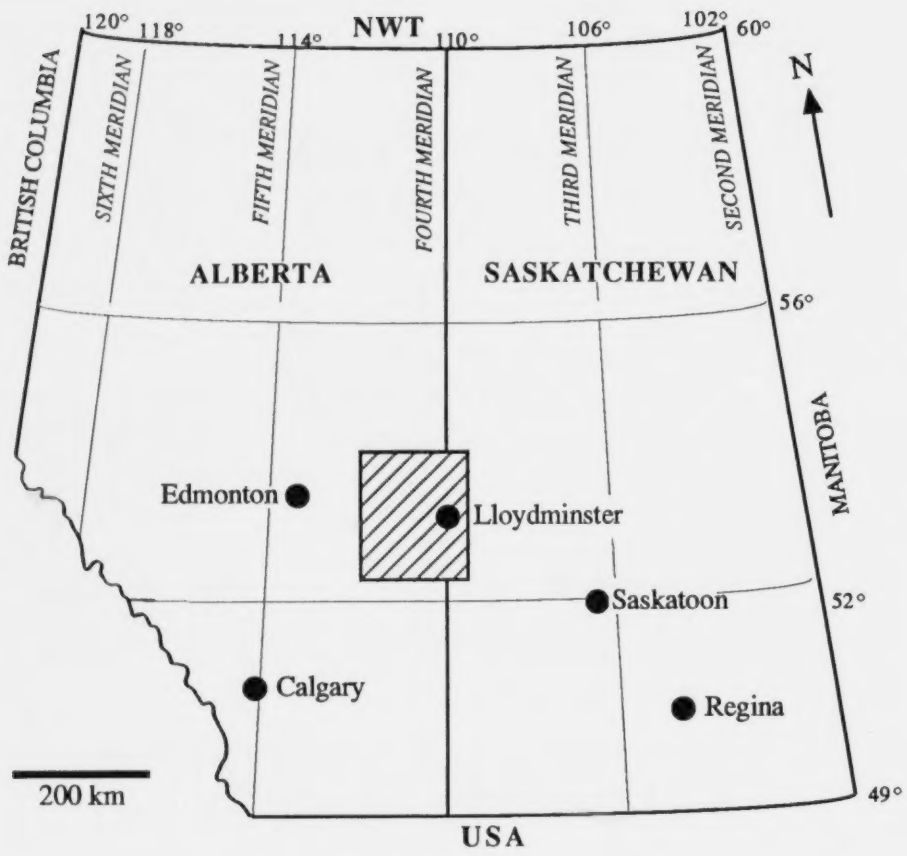


Figure 2.1. Location of the study area.

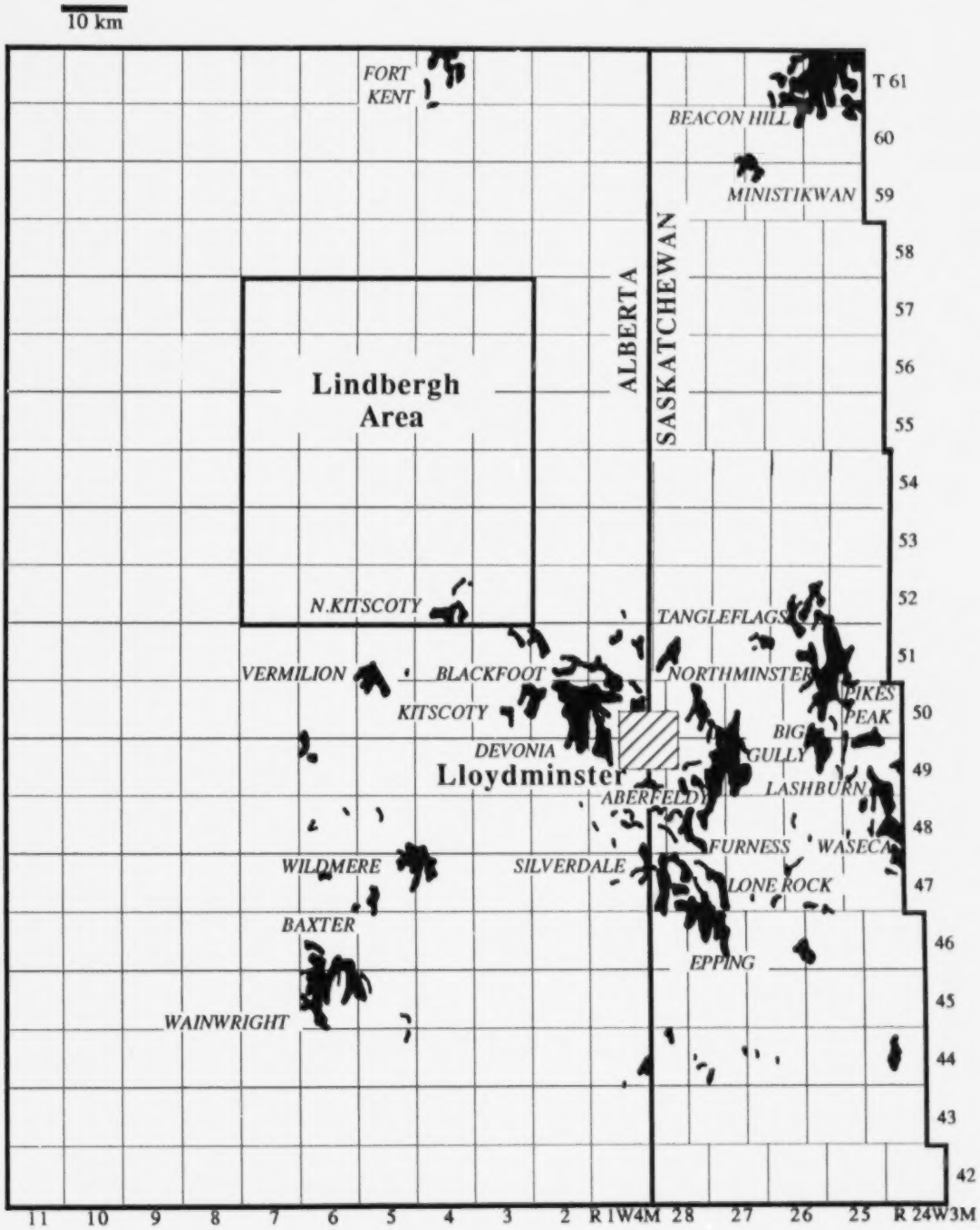


Figure 2.2. Outline of the Lloydminter study area illustrating the major oil fields of the region. Most of the samples were obtained from the Lindbergh section.

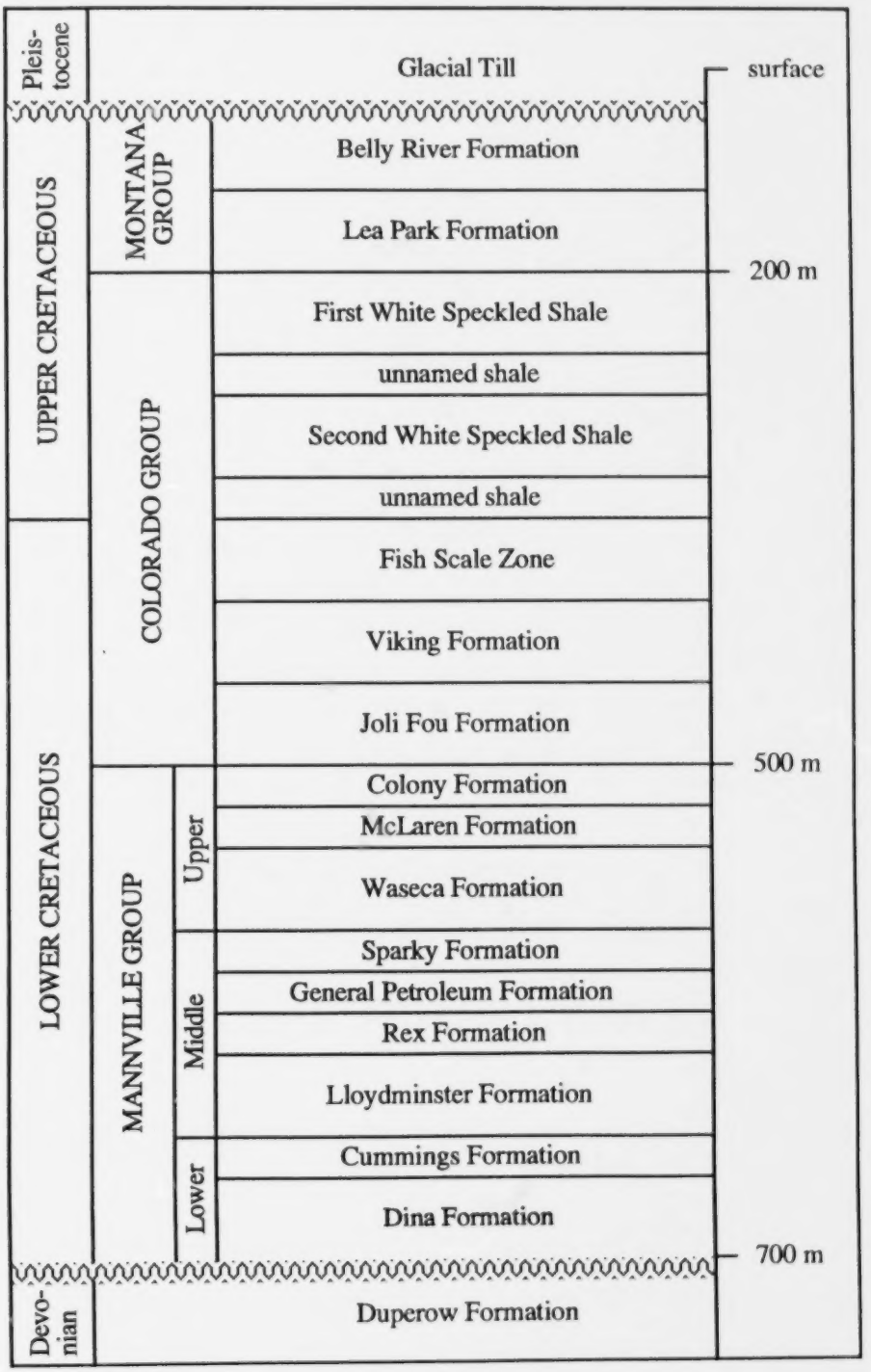
resulted from draping and compaction over the underlying relatively flat pre-Cretaceous basement (White and Shultz, 1977). However, localized complex structures have resulted from the salt solution collapse of underlying Paleozoic evaporites (White and Shultz, 1977; Putnam, 1983; van Hulten and Smith, 1984). These local features tend to dominate the regional pattern.

The Mannville Group unconformably overlies eroded, gently southwesterly-dipping Devonian carbonates and minor clastics of the Duperow Formation (White and Shultz, 1977; Putnam, 1981; MacEachern, 1984; Smith, 1984; Zaitlin and Shultz, 1984). In the Lloydminster region, post-Mannville tilting to the southwest has enhanced the structural dip on subcropping Paleozoic strata (van Hulten and Smith, 1984). The Mannville is sharply overlain by marine shales of the Joli Fou Formation of the Cretaceous Colorado Group (White and Shultz, 1977; Putnam, 1981; MacEachern, 1984; Smith, 1984). The contact between the Mannville Group and the basal unit of the Colorado Group has been described as conformable by some (Vigrass, 1968; White and Shultz, 1977) and disconformable by others (Christopher, 1974; Putnam, 1983; Smith, 1984; Zaitlin and Shultz, 1984; Jocksch *et al.*, 1993).

2.3 Stratigraphy

In the Lloydminster region, the Mannville Group comprises several sand-shale cycles, some of which are capped by coal beds (Haidl, 1981; van Hulten and Smith, 1984; Putnam and Klovan, 1987). The extreme lateral variation, the repetitive vertical sequence lithology and the lack of regional or widespread marker beds (Haidl, 1981) render geologic interpretation difficult. The only good geologic information for most wells comes from geophysical well logs (Haidl, 1981). The interpretation of electric logs led to the division of the Mannville Group into nine informal stratigraphic units (Table 2.1), each characterized locally by the development of one sand considered a potential reservoir rock (Gross, 1981; MacEachern, 1984). The recognized sands, in ascending

Table 2.1. Stratigraphic nomenclature of the Mannville and Colorado Groups in the Lloydminster area (modified after Orr *et al*., 1977).



order, are the Dina, Cummings, Lloydminster, Rex, General Petroleum, Sparky, Waseca, McLaren and Colony. These units were later termed members by Vigrass (1977) and formations by Orr *et al.* (1977). Vigrass (1977) and Orr *et al.* (1977) both placed their stratigraphic boundaries at the top of the sandstones (Smith, 1984; Smith *et al.*, 1984). MacCallum (1979) initiated the use of shale and coal marker beds in correlating contacts.

The thickness of the Mannville Group varies substantially throughout the Lloydminster region (75 - 250 m) (White and Shultz, 1977; Tilley and Last, 1981). Along with a regional thinning of the sediments toward the southwest, there exists local thinning over hills on the Paleozoic erosional surface (White and Shultz, 1977). The formation sands, though persistent, thin and thicken notably over short distances and exhibit great change in the thickness and number of interbeds. Thus, electric log signatures are rarely readily identifiable, and correlation over long distances is questionable. The recognition of individual sands is further obscured by the notable changes in overall Mannville thickness (White and Shultz, 1977).

The difficulty encountered in recognizing individual sands and in defining unit boundaries has created a lack of nomenclatural consistency. The most common stratigraphic nomenclature applied to the Mannville Group in the Lloydminster area is that described by Vigrass (1977) and by Orr *et al.* (1977). (This paper will follow that outlined by Orr *et al.* (1977).) There are, however, terminological discrepancies between various regions (i.e. Alberta versus Saskatchewan) and companies (i.e. Husky Oil Operations Limited versus Amoco Canada Petroleum Company Limited) (Table 2.2). Even within the same geographical locale, different names are often applied to apparently equivalent strata. Such discrepancies are a reminder of the informal nature of the Mannville Group stratigraphic subdivisions.

The Mannville Group is overlain by the Joli Fou Formation, the basal unit of the Colorado Group (Table 2.1). With the exception of the Viking Formation beach and blanket sandstone bodies, the Cretaceous marine sequences overlying the Mannville

Table 2.2. Stratigraphic correlation chart of Mannville strata of the Lloydminster region.

	HUSKY		AMOCO
	LLOYDMINSTER, Saskatchewan	COLD LAKE, Alberta	
MANNVILLE GROUP	Colony	Upper Grand Rapids	Colony
	McLaren		
	Waseca	Lower Grand Rapids	Sparky
	Sparky		
	General Petroleum		General Petroleum
	Rex		
	Lloydminster	Clearwater	Clearwater
	Cummings	Wabiskaw	Cummings
	Dina	McMurray	Dina/McMurray

Group zones in the Lloydminster region are of limited commercial potential, and thus, have been largely ignored. The Colorado Group stratigraphic subdivisions are more precise than those of the Mannville as the group contains widespread correlatable marker beds. The shaley sands of the Viking are overlain by the graded sandstones, made of fish-skeletal debris, and muds comprising the Fish Scale Zone (Simpson, 1984). The upper portion of the Colorado Group consists of two main calcareous marker beds, the Lower (Second) and the Upper (First) White Speckled Shales, which are separated by an unnamed non-calcareous shale sequence (Simpson, 1984). The Colorado Group is overlain by a thick sequence of marine shales comprising the Lea Park Formation which is, in turn, capped by sandstones of the Belly River Formation and glacial till (Table 2.1).

2.4 Lithology

In the Lloydminster area, the Mannville Group is a 75 - 250 m thick (White and Shultz, 1977; Tilley and Last, 1981) clastic body comprised of a complex arrangement of poorly consolidated sands, shales, interbedded sands and shales, minor coals and rare conglomerates and breccias (MacEachern, 1984, 1989). The sands are predominantly fine-grained quartz. The sandstones commonly exhibit cross-bedding and are usually quite porous. The shales are grey in colour and may contain carbonaceous flakes. Coal occurs in beds as well as pieces scattered through strata of other lithology. Ironstones, conglomerates and breccias are sporadically distributed in places (White and Shultz, 1977).

There is no single lithology or pattern of lithologies which is representative of a single formation (Haidl, 1981). The repetitive sand-shale cycles making up the Mannville Group typically consist of a basal mudstone, or relatively muddy zone, overlain by a coarsening upward sandstone which is in turn capped by a mudstone, muddy zone or coal (Putnam and Klovan, 1987). Sets of these cycles correspond to the formations comprising the Mannville Group.

The Mannville Group formation sands are described as sheet-like sands (van Hulten *et al*., 1984). The "blanket" sands are termed the "regional facies" (Gross, 1981; van Hulten and Smith, 1984). These cyclic sequences are interpreted to be wave-formed sediments (Putnam and Klovan, 1987). Each of the areally extensive sheet sand bodies characterizing the Mannville Group subdivisions is dissected in places by non-cyclic deposits (Putnam and Klovan, 1987). The non-cyclic sediments represent channel fills (Putnam and Klovan, 1987). The thick sand and shale channels are the "areally-restricted facies," and they occur in each interval of the Mannville sequence (Gross, 1981; Putnam, 1983).

The stratigraphic section above the Mannville Group in the Lloydminster area is the 285 m thick, dominantly agrillaceous Colorado Group. The Lower to Upper Cretaceous reservoirs are composed of marine shales, shaley chalks, siltstones and sandstones (Jocksch *et al.*, 1993). The Lea Park marine shales form the caprocks for the underlying Colorado Group source rocks and reservoirs. The Belly River Formation, an interfingering succession of deltaic and marine sandstones, laterally grades into the underlying Lea Park Formation. The formation thickness varies greatly due to Pleistocene and Recent erosion. The sandstones of this shallow formation are a source of potable water in the Lloydminster area but are gas-bearing to the south and west.

2.5 Depositional Environment

Deposition of the Mannville Group in east-central Alberta and west-central Saskatchewan was influenced by the tectonics of deep seated basement rocks, a series of northwest-trending Paleozoic carbonates located in the central plains, evaporite dissolution within the depositional basin, and eustatic changes within the Boreal and Gulfian seas (Putnam, 1982; McPhee, 1994).

The Lower Mannville formations (Dina and Cummings) occupy the lows between the northwest-trending Paleozoic carbonate ridges (Putnam, 1982). The siliceous

sandstones are interpreted to be valley-fill deposits of a agrading north-flowing fluvial system (Putnam, 1982). The middle units (Lloydminster, Rex, General Petroleum and Sparky) are the typical sheet-like sands which are truncated by sand or shale-filled channels. These facies are said to have been deposited in transgressive followed by regressive wave-dominated paralic environments. Continued regressive sedimentation in an areally extensive, north-flowing anastomosed fluvial network created the thicker channel deposits observed in the Upper Mannville formations (Waseca, McLaren and Colony).

The deposition of Mannville sediment in the area around Lloydminster was terminated by a major transgression which deposited the widespread marine shales of the overlying Colorado Group (Putnam, 1982). Deposition of the Lea Park non-calcareous shale began with a rise of a land barrier in the Northwest Territories, restricting the seas to Alberta (Edmonton Geological Society, 1968).

2.6 Hydrocarbon Association

Hydrocarbons are found in both the blanket-type and channel sandstones of the Mannville Group (Putnam, 1983). Though the individual pool traps are mainly stratigraphic in origin, the overall petroleum distribution is also related to structure (White and Shultz, 1977; Smith *et al.*, 1984). The thickest sandstones are the best reservoir rocks. They are also less compactible, thereby forming structural highs. Thus, the majority of the established and prospective pools or accumulations are associated with gentle highs (White and Shultz, 1977; Putnam, 1983). No important accumulations occur in structurally low sands (White and Shultz, 1977).

There are two main hydrocarbon trapping mechanisms within the geology of the Lloydminster region (Putnam, 1983; Smith *et al.*, 1984). First, regional facies sands and silts abut up-dip against shale-filled channel facies thus forming a permeability barrier. Second, the general lateral facies change in an up-dip direction forms a barrier in itself.

There is a regional southwesterly dip, and the channel deposits dominantly trend northwest by southeast. Toward the northeast the channel sandstones grade into sheet sands, silts and coals. The sheetlike sandstones, in turn, pinch out further toward the northeast. Thus, the up-dip lateral facies changes form a hydrocarbon trap.

Source rocks occur in the Fish Scales and White Speckled Shales. Though commercial gas is quite rare in the upper formations of the Colorado Group in the Lloydminster region, small gas blows (up to 5000 m^3/day) are common (Jocksch *et al.*, 1993).

2.7 Summary

The Lloydminster area of Alberta and Saskatchewan is characterized by a high density of shallow wells recovering from the heavy oil and gas held in the poorly consolidated sands, silts, shales and minor coals and conglomerates of the Lower Cretaceous Mannville Group. This group has been informally subdivided into nine units whose nomenclature has evolved both through academic and industry use. The stratigraphic nomenclature most often applied to the Mannville reservoirs in the Lloydminster region is: Dina, Cummings, Lloydminster, Rex, General Petroleum, Sparky, Waseca, McLaren and Colony. The Mannville Group reserves are sharply overlain by marine shales of the Colorado Group which, due to their lesser commercial potential, have received less attention. Portions of the Colorado Group and overlying sediments, however, contain organic-rich source rocks which have generated bacteriogenic methane in the Fish Scales and White Speckled Shale Formations. There also exist both conventional and non-conventional gas reservoirs in the Viking, White Speckled Shale and Belly River Formations.

3. PRODUCTION HORIZON GASES

3.1 Isotopic Signatures

The carbon and hydrogen isotope compositions of the Lloydminster region production gases are listed in Appendix 2, and the data are summarized for each formation in Figures 3.1 and 3.2. The horizons are arranged according to stratigraphic depth and can be grouped into two units: the Devonian and the Mannville Group strata, and the Colorado Group strata.

The methane component of all the analyzed Devonian and Mannville Group formation gases is highly depleted in ^{13}C ($\delta^{13}C_1$(PDB) ≈ -70 to -50 ‰). The trace ethane, propane and butane constituents of these deeper natural gases are isotopically heavier, their $\delta^{13}C$ values averaging -27 ‰, -21 ‰ and -23 ‰, respectively. These $\delta^{13}C$ values are higher than those observed in petroleum associated gases, but such ^{13}C-enrichment can be seen in coal gases (Chung and Sackett, 1978). The ^{13}C content of the carbon dioxide component is highly variable ($\delta^{13}CO_2$(PDB) ≈ -30 to -1 ‰). The isotopic composition ranges between that observed in soil CO_2 (Deines, 1980) and that of atmospheric CO_2 (Cerling *et al.*, 1991). The hydrogen isotope composition of the production gas constituents is more scattered (Figure 3.2). The range of δD(SMOW) values is -374 to -212 ‰ for methane, -296 to -90 ‰ for ethane, -298 to -44 ‰ for propane and -332 to -163 ‰ for butane. The wide spread in the deuterium content of the natural gas components may be a result of water from the collected sample eluting throughout the gas chromatograph spectrum and mixing with the separated hydrocarbons.

The homogeneity of the isotopic signatures of the production gases was tested by determining the variation of the isotope composition of the Cummings Formation gas within the Lindbergh field (Figure 3.3). The carbon isotope content of Cummings gas does vary over the region, but the general signature of ^{13}C-depleted methane and ^{13}C-rich higher hydrocarbons holds throughout the region. There is no obvious trend of ^{13}C-

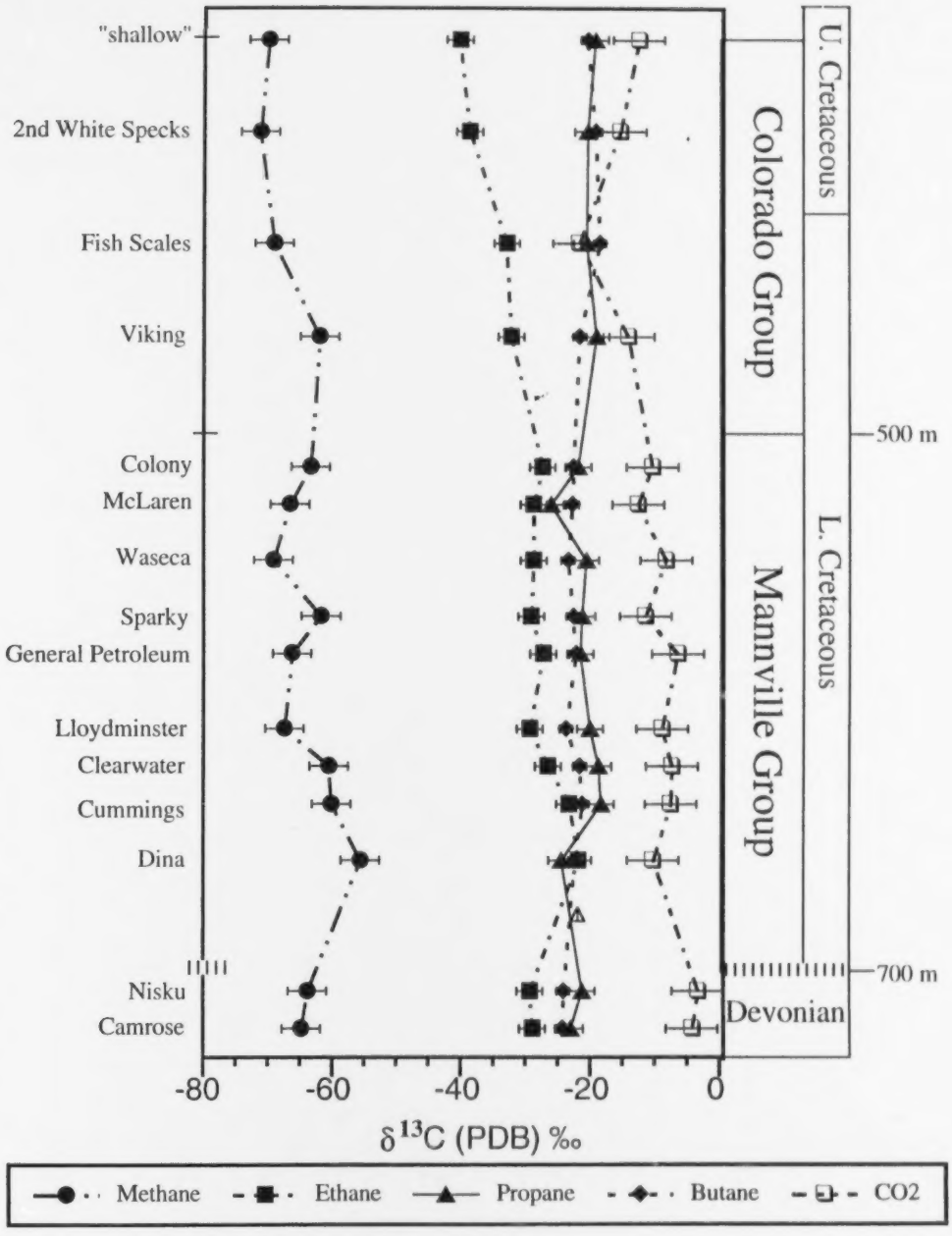


Figure 3.1. Summary of the carbon isotope composition of solution gases of the Lloydminster heavy oil field. (The "shallow" formation is located somewhere above the Second White Speckled Shale. The specific horizon sampled is unclear.)

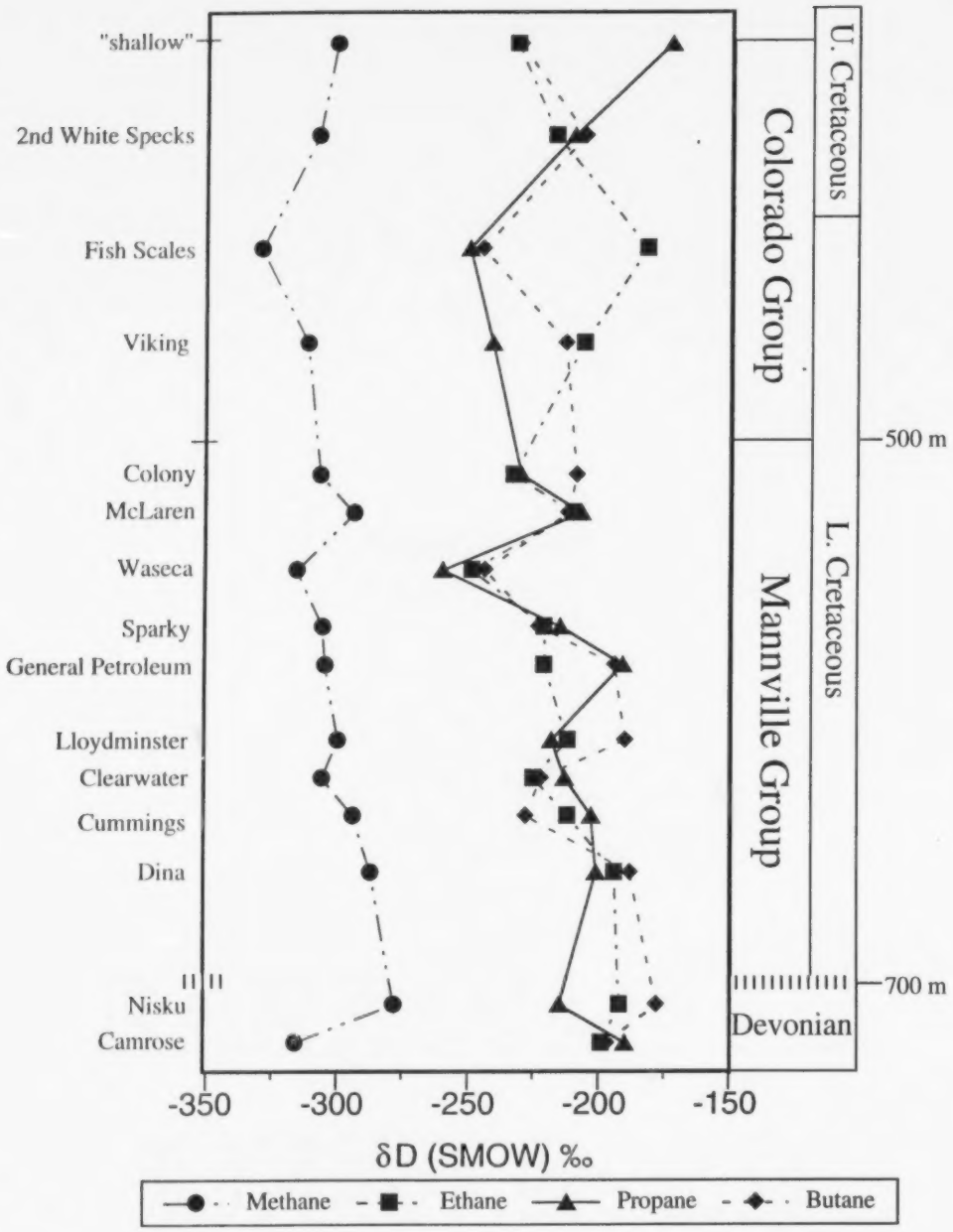


Figure 3.2. Summary of the average hydrogen isotope composition of solution gases of the Lloydminster heavy oil field. (The "shallow" formation is located somewhere above the Second White Speckled Shale. The specific horizon sampled is unclear.) The standard deviation of the δD values is 23 ‰ for methane, 38 ‰ for ethane, 38 ‰ for propane and 30 ‰ for butane.

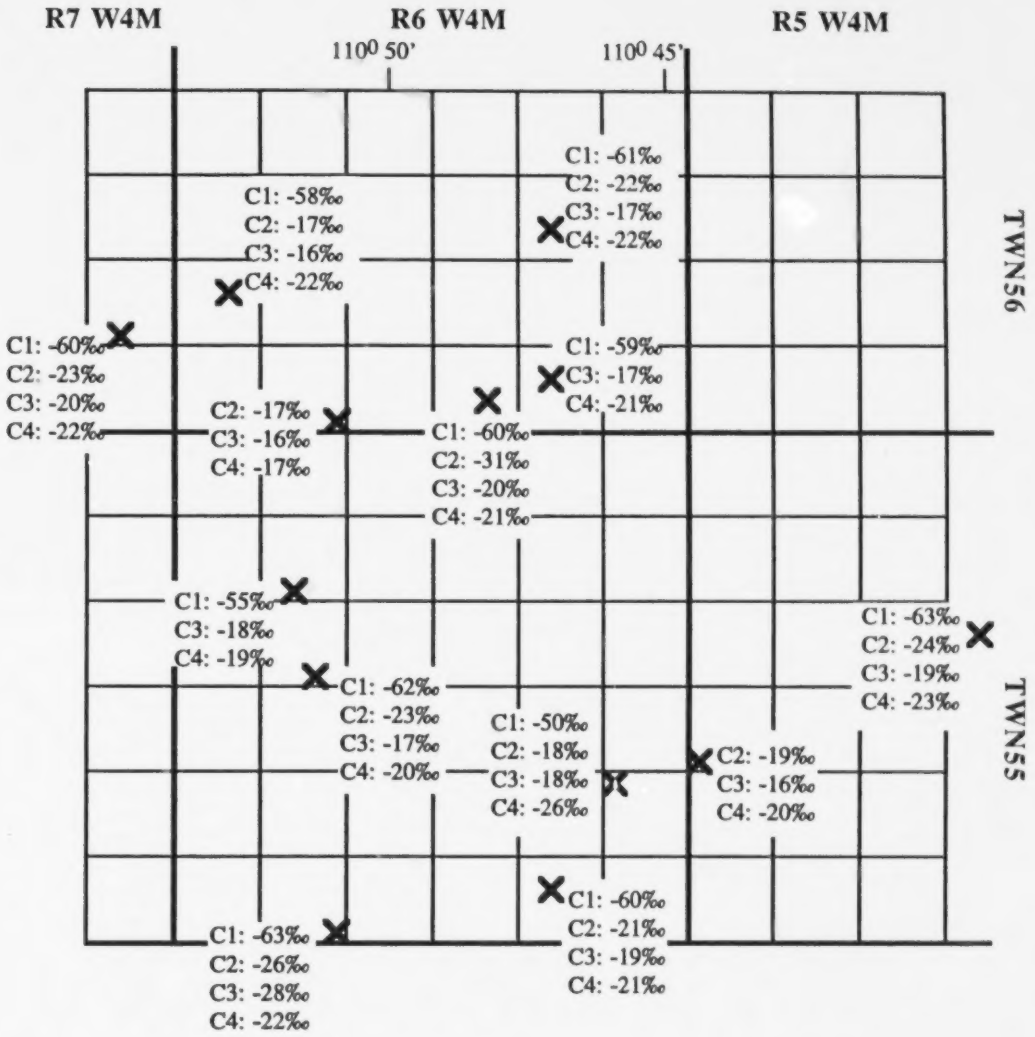


Figure 3.3. Test of regional homogeneity: Carbon isotope composition of Cummings Formation gas in the Lindbergh area. The ^{13}C content of Cummings Formation gas is: $\delta^{13}C_1 = -60 \pm 5$ ‰, $\delta^{13}C_2 = -23 \pm 5$ ‰, $\delta^{13}C_3 = -18 \pm 3$ ‰ and $\delta^{13}C_4 = -21 \pm 2$ ‰. (Note: The standard deviations of the Cummings gas δ values are greater than those observed in other formations. Pooled residual variance calculations of the isotope content of formation gases give standard deviation values of 3 ‰ for methane, 2 ‰ for ethane, 2 ‰ for propane and 1 ‰ for butane.)

enrichment or depletion with direction.

The shallower Colorado Group production horizon gases possess a different isotopic signature. In general, the gas of these strata is isotopically lighter than that of the underlying Mannville Group and Devonian formations (Figure 3.1). The ^{13}C content of Viking gas ethane and CO_2 is slightly less than that of the deeper horizon gases ($\delta^{13}C_{2(PDB)} \approx -32$ ‰ and $\delta^{13}CO_{2(PDB)} \approx -14$ ‰). Methane, ethane and CO_2 of the Fish Scales Formation are notably depleted in ^{13}C compared to their Mannville Group counterparts ($\delta^{13}C_{1(PDB)} \approx -69$ ‰, $\delta^{13}C_{2(PDB)} \approx -33$ ‰ and $\delta^{13}CO_{2(PDB)} \approx -22$ ‰). The Second White Speckled Shale gas is even further depleted in ^{13}C ($\delta^{13}C_{1(PDB)} \approx -71$ ‰ and $\delta^{13}C_{2(PDB)} \approx -39$ ‰). The deuterium content of the Colorado Group gases is slightly less than that of the deeper strata gases (Figure 3.2), with δD values ranging from -342 to -300 ‰ for methane, -232 to -175 ‰ for ethane, -284 to -189 ‰ for propane and -288 to -198 ‰ for butane.

There appears to be a weak correlation of ^{13}C-enrichment with depth in the methane, ethane and CO_2 components. Such trends have been observed in other natural gas fields (Hitchon *et al.*, 1975; Deines, 1980), including the Devonian strata of Alberta (Krouse, 1980). If the change in δ values were attributable to a diffusion-type process, the ^{13}C content of all of the gas components would shift in the same direction (albeit at different rates). However, as the methane, ethane, and CO_2 get isotopically heavier with depth and the propane and butane get lighter with depth, some selective process is altering the gas' isotopic composition.

3.2 Gas Field Source Inference

The isotopic data of the formation gases can be compared with published studies to determine the source of the solution gas associated with the heavy oils in the Lloydminster region. Though methane has the largest $\delta^{13}C$ range of any naturally occurring C-bearing compound ($\delta^{13}C_{1(PDB)} \approx -90$ to 0 ‰) (Deines, 1980; Edwards and

Durucan, 1991), the different categories of methane have distinct $\delta^{13}C$ ranges (Figure 3.4). The ^{13}C content of liquid petroleum components is similar to their source organic material (Edwards and Durucan, 1991), but the isotope composition of gaseous hydrocarbons is significantly lighter than their source matter.

Primary natural gases are generated through a variety of diverse processes including microbial action, thermogenesis, hydrothermal/geothermal activity and primordial or mantle emissions (Table 1.1). Natural gases are, however, primarily produced by the microbial and thermal degradation of organic material. In general, the ^{13}C concentration in natural gas increases with increasing maturity (Deines, 1980; Schoell, 1980; Coleman *et al.*, 1981; Balabane *et al.*, 1987; Edwards and Durucan, 1991). There is a greater isotopic variation in deuterium composition than in corresponding carbon values (Whiticar *et al.*, 1985).

The production of natural gas by bacteria commonly occurs in oil reservoirs, and it is often a component of oil field gas (Whiticar, 1994). Such immature gases are almost exclusively methane (usually <1 % C_{2+}) (Whiticar, 1994) and have low $\delta^{13}C$ and δD values ($\delta^{13}C_{1(PDB)} \approx$ -90 to -50 ‰ (Deines, 1980; Stahl *et al.*, 1981; Edwards and Durucan, 1991) and $\delta D_{(SMOW)} \approx$ -550 to -175 ‰ (Schoell, 1980; Whiticar, 1994)) (Figure 3.4). Natural gas genesis by microbial action can occur by two general pathways. The carbonate reduction pathway is predominant in marine environments (Balabane *et al.*, 1987; Grossman *et al.*, 1989; Whiticar, 1994) and can be illustrated by the general reduction reaction:

$$CO_2 + 4H_2 \Rightarrow CH_4 + 2H_2O.$$

Methyl-type fermentation is more common in freshwater environments (Whiticar, 1994), and the basic reaction illustrating this pathway using acetate as an example is (Balabane *et al.*, 1987; Grossman *et al.*, 1989; Whiticar, 1994):

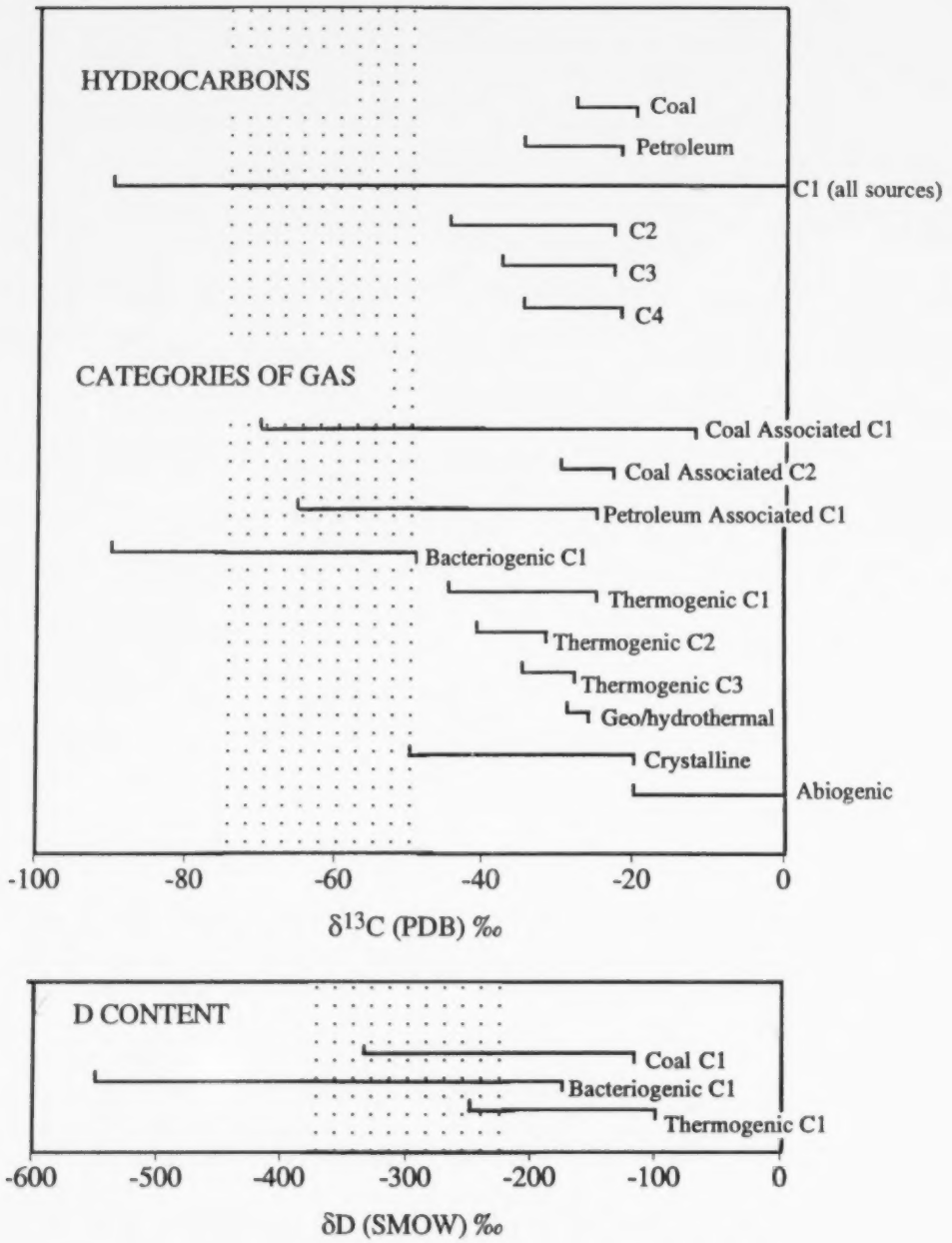


Figure 3.4. Carbon and hydrogen isotope composition ranges of C-bearing components of natural gases from various sources. Data from Deines (1980), Schoell (1980), Stahl *et al*. (1981), Hallam *et al*. (1990), Edwards and Durucan (1991), Jenden *et al*. (1993), Rice (1993) and Whiticar (1994). (The stippled region is the isotope content of the C_1 component of Lloydminster area gas.)

$$^{*}CH_3COOH \Rightarrow {}^{*}CH_4 + CO_2.$$

(The asterisk (*) indicates the transfer of the methyl position to methane.) The enrichment of dry bacterially derived gases in ^{12}C results from the higher binding energies of ^{12}C - ^{13}C bonds in comparison to ^{12}C - ^{12}C bonds (Deines, 1980; Stahl *et al.*, 1981; Balabane *et al.*, 1987). The preferential use of the organic substrate ^{12}C by microbes causes a systematic enrichment in ^{13}C in the residual organic material. Unlike what is noted for the carbon isotope content, the D/H ratio of bacteriogenic gas is not a function of the amount of gas produced (Balabane *et al.*, 1987). The concentration of deuterium in bacteriogenic gas is dependent on the associated water D/H ratio (Schoell, 1980):

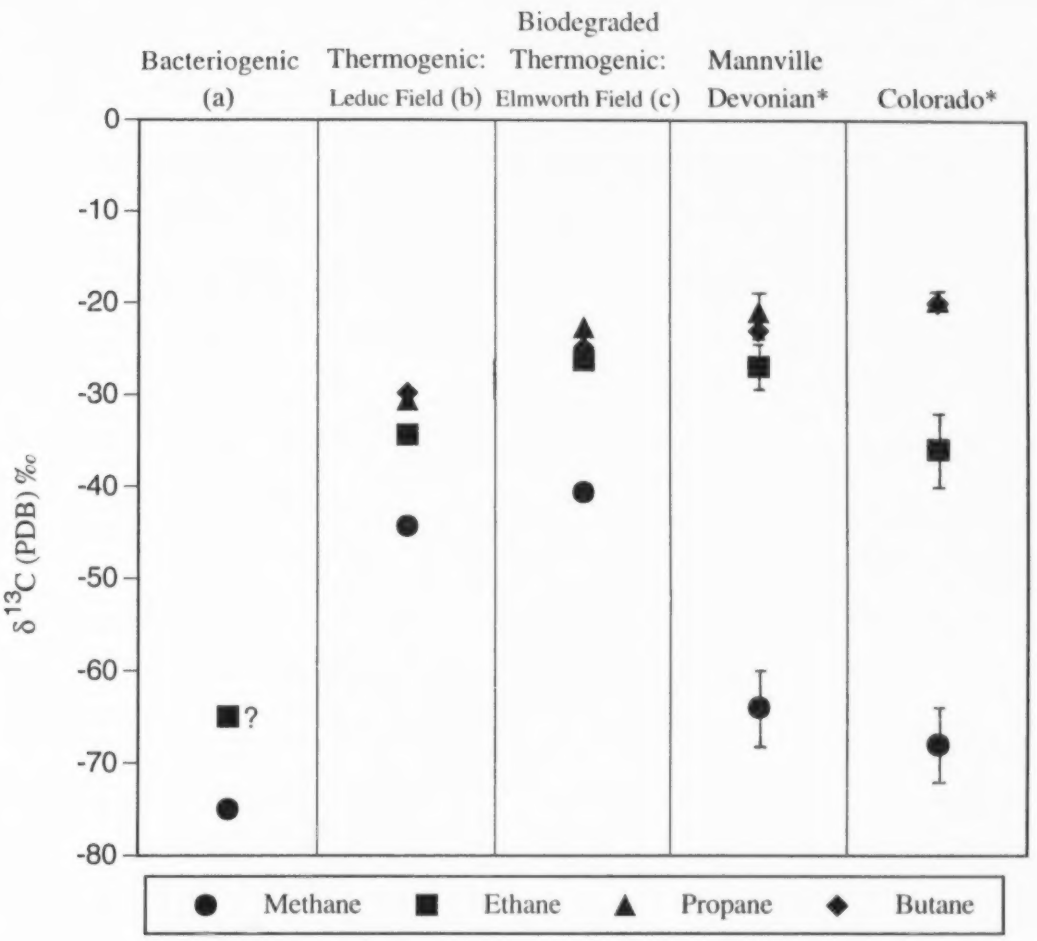
$$\delta D\, C_1\,(\text{SMOW}) = \delta D \text{ water} - (160 \pm 10\,‰).$$

During the thermal degradation of organic material, various short-chained hydrocarbons are broken off the substrate and saturated to form the light hydrocarbons of natural gas (Whiticar, 1994). The carbon isotope composition of thermogenic gas is therefore dependent on the type of source material as well as the degree of thermal transformation (Schoell, 1980; Hallam *et al.*, 1990). Dry mature gases produced in the oil window generally have methane $\delta^{13}C$ values between -45 and -25 ‰ (Stahl *et al.*, 1981; Hallam *et al.*, 1990; Edwards and Durucan, 1991; Jenden *et al.*, 1993) (Figure 3.4). There is a much smaller variation in the carbon isotope composition of the higher hydrocarbon components of thermogenic gas (Figure 3.4). In co-generated gas there is a progressive enrichment in ^{13}C with increasing hydrocarbon chain length (Deines, 1980; James, 1983; James and Burns, 1984). The D/H ratios of dry thermogenic gases are also a reflection of the maturity of the source material (Schoell, 1980), and the δD values increase with C number (Whiticar *et al.*, 1985). The normal δD range for the methane

component of dry thermogenic gas is -250 to -100 ‰ (Schoell, 1980; Whiticar, 1994) (Figure 3.4).

Biodegradation of natural gas can greatly alter its isotopic composition. Bacterial alteration of natural gases extends in the range of C_1 to C_4, most often selectively degrading the higher hydrocarbons (James and Burns, 1984). Initially, propane appears to be preferentially biodegraded (James and Burns, 1984; James, 1990) causing a violation of the predicted sequence of ^{13}C enrichment ($C_1<C_2<C_3<C_4$). Bacteria consuming the gas preferentially oxidize the light isotopes, ^{12}C and H, leaving an isotopically heavier residual gas (Coleman *et al.*, 1981; Balabane *et al.*, 1987). Extensive biodegradation of a bacteriogenic gas can enrich the residual gas in ^{13}C to the extent of it gaining an isotope composition similar to thermogenic gas (Coleman *et al.*, 1981; Balabane *et al.*, 1987). The likely reaction product of biodegradation is CO_2 which, due to its solubility, may be easily removed by solution in groundwaters or by precipitation as carbonates (James and Burns, 1984). In addition, the produced CO_2 may be mixed with that of other sources. Thus, not all biodegraded gases possess unusually ^{13}C-depleted CO_2.

Figure 3.5 compares the average carbon isotope composition of the sampled Devonian, Mannville and Colorado Group gases to that of natural gases of different origins (bacteriogenic, thermogenic and biodegraded thermogenic). The methane component of the solution gases is very depleted in ^{13}C ($\delta^{13}C_1$ Mannville (PDB) ≈ -64 ‰ and $\delta^{13}C_1$ Colorado (PDB) ≈ -68 ‰) similar to what is observed in bacteriogenic gases (Figure 3.5). The very low deuterium content of the solution gas methane is expected in bacteriogenic gases generated in the presence of isotopically light formation water. The $\delta D_{(SMOW)}$ value of the Cummings Formation water ranged between -110 and -100 ‰. According to Schoell's equation (1980), the concentration of deuterium in bacteriogenic methane generated in such water should range between -265 ± 15 ‰. The average Cummings methane $\delta D_{(SMOW)}$ value, -294 ‰, falls just outside the predicted range for



(a) SOURCE: Whiticar (1994)

(b) SOURCE: James (1990)

(c) SOURCE: James and Burns (1984)

? It is suggested that bacteria can produce ethane, but the isotopic composition of such ethane is unknown.

* All formations were weighted equally in the determination of the average isotope composition of the solution gases.

Figure 3.5. Comparison of the carbon isotope composition of Lloydminster area solution gases and other gas types. The $\delta^{13}C$ values of the CO_2 component are not plotted due to its solubility and the common mixing of CO_2 from different sources.

bacteriogenic gas generated in the presence of such water. (Stratigraphically shallower methane tends to have lower δD values (Figure 3.2) as the D/H ratio in the formation waters are usually D-enriched with respect to surface waters.) Though the range in methane $^{13}C/^{12}C$ ratios is wide ($\delta^{13}C_{1(PDB)} \approx$ -75 to -50 ‰), it correlates with that Feux (1977) noted in certain Albertan oil fields. He noted a relationship between the $^{13}C/^{12}C$ ratio of methane and gas wetness (C_{2+} content) and attributed the observation to the mixing of small quantities of wet thermogenic gas (which is known to be isotopically heavier) with bacteriogenic reservoirs. James (1983) used the isotopic composition of the higher hydrocarbons (C_2, C_3 and C_4) to prove Feux's mixed gas concept.

Ethane of the deeper production horizons has an isotopic signature ($\delta^{13}C_{2(PDB)} \approx$ -27 ‰) like the biodegraded thermogenic gas of the Elmworth field ($\delta^{13}C_{2(PDB)} \approx$ -26 ‰) (James and Burns, 1984) (Figure 3.5). The reverse $^{13}C/^{12}C$ partitioning between the propane and butane observed in many of the Lloydminster area solution gases (Figure 3.1) is also observed in the Elmworth gas (Figure 3.5). The reversal is a reflection of the occurrence of non-equilibrium processes, namely biodegradation. Figure 3.6 further illustrates the effect kinetic processes have had on the partitioning of ^{13}C between the hydrocarbons. In co-generated gases, the fractionation between methane and ethane is proportional to that between ethane and propane. The partitioning observed for the Devonian, Mannville and Colorado Group formation gases opposes equilibrium-generated trends, reflecting the non-equilibrium nature of the ^{13}C partitioning between the gas components (Figure 3.6).

The Colorado Group ethane is unusually depleted in ^{13}C ($\delta^{13}C_{2(PDB)} \approx$ -44 to -32 ‰), the origin of which is unclear (Figure 3.5). Such isotopically light ethane can result from mild thermogenesis (James, 1983), but proportionally ^{13}C-depleted propane and butane would also be observed. The $^{13}C/^{12}C$ ratios of the Colorado Group formation gas propane and butane are too great to be representative of immature thermogenic gas. Similarly, any physical process such as diffusion which would partition the ethane carbon

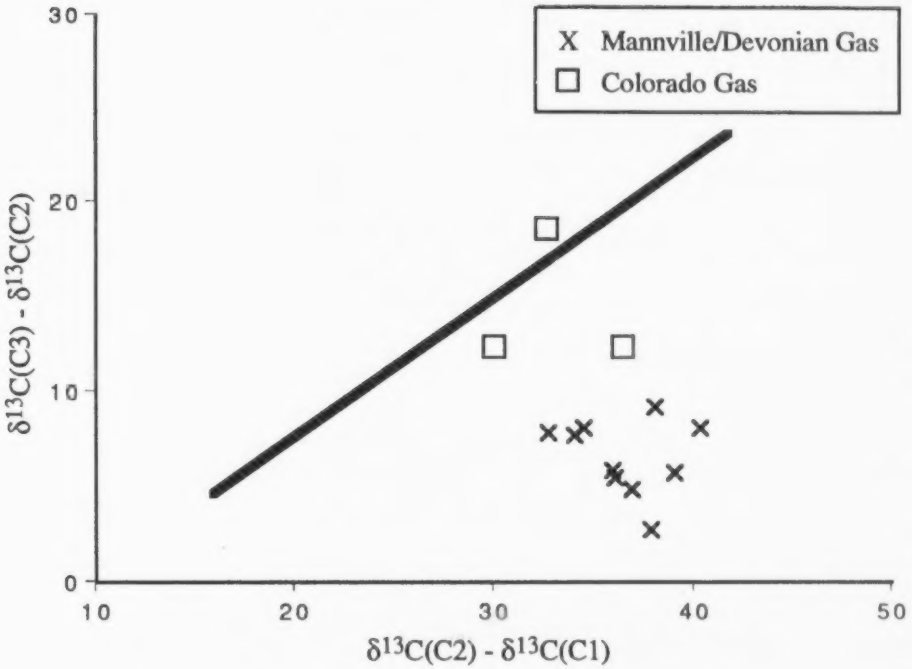


Figure 3.6. ^{13}C partitioning between methane and ethane versus that between ethane and propane in the Lloydminster area solution gases. Thermogenic gases would plot near the thick line, the partitioning decreasing with increasing maturity.

composition would proportionally alter the propane and butane isotopic signature. The microbial alteration which appears to have increased the $\delta^{13}C$ of propane and butane would have also enriched the ethane in ^{13}C as seen in the Elmworth field (Figure 3.5). Consequently, the origin of the ^{13}C-depleted ethane must post-date the bacterial degradation of the thermogenic gas component. Perhaps the ^{12}C-rich ethane is derived from ethanogenesis. A bacteriogenic origin for the ethane is supported by the accompanying drop in the ^{13}C content of methane of the shallower formations ($\delta^{13}C_1$(PDB) ≈ -75 to -62 ‰) compared to the deeper gases ($\delta^{13}C_1$(PDB) ≈ -70 to -50 ‰).

The source of the gas associated with the heavy oils in the Lloydminster region is predominantly bacteriogenic, but variably mixed with biodegraded thermogenic gas (and perhaps some coal gas) (Figure 3.7). The dominant bacteriogenic methane component may have been produced from the degradation of the heavy oil of the region.

3.3 Isotopic Fingerprinting of Formation Gases

Slight variations in the degradation of oil and in the amounts of mixing give rise to unique isotope signatures in some of the production horizon gases of the Lloydminster region. For example, McLaren gas has propane of relatively low $\delta^{13}C$ value (Figure 3.1). Waseca gas methane is very ^{13}C-depleted; Dina methane and ethane are enriched in ^{13}C. Devonian and Mannville Group formation gases are isotopically heavier than the shallower Colorado Group gases. These isotopic fingerprints are important in the deduction of the source of migrating gas observed around wells in the Lloydminster area.

3.4 Summary

The dominant methane component of all of the solution gases of the Lloydminster heavy oil field is very depleted in ^{13}C and D ($\delta^{13}C_1$(PDB) ≈ -75 to -50 ‰ and δD(SMOW) ≈ -374 to -212 ‰), indicative of a bacterial origin. The $\delta^{13}C$ values of the trace higher hydrocarbon constituents are relatively high, and often the propane

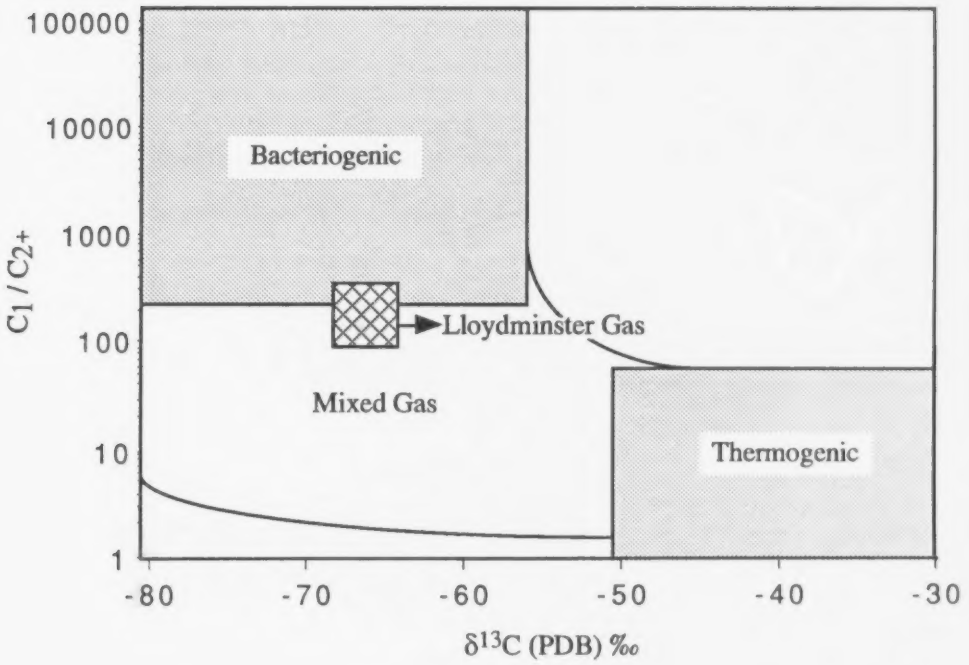


Figure 3.7. The chemistry and the isotopic composition of the Lloydminster area solution gases identify the gases as predominantly bacteriogenic in origin but mixed with small amounts of biodegraded thermogenic gas (modified after Coleman *et al.*, 1981 and Whiticar, 1994).

component is more enriched in ^{13}C than the butane fraction. This reverse $^{13}C/^{12}C$ partitioning opposes equilibrium generated trends and is a reflection of extensive biodegradation. Thus, the Lloydminster region solution gases are mixtures of mostly bacteriogenic gas and small amounts of biodegraded thermogenic gas.

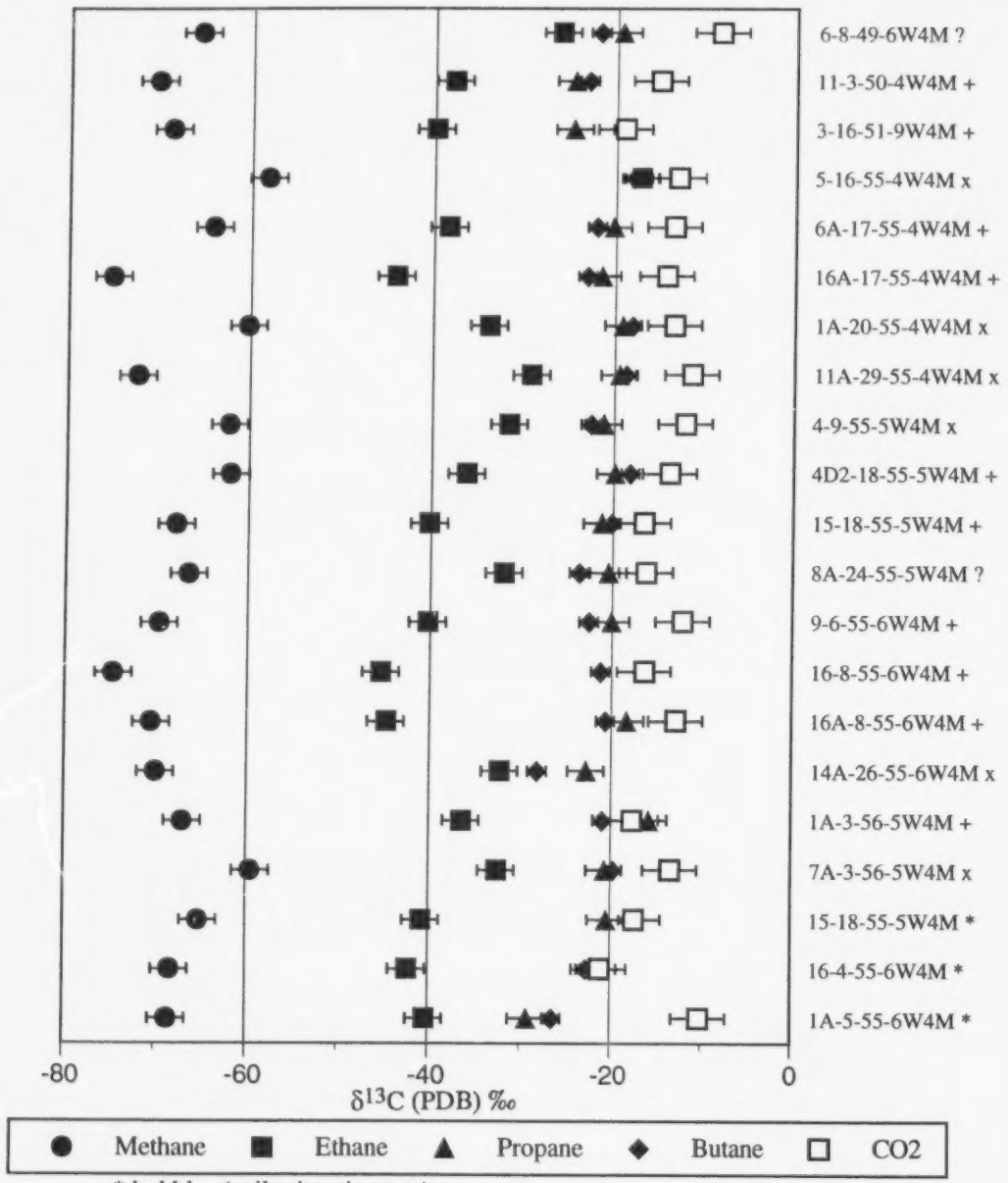
Variations in the amount of mixing and degradation give rise to unique isotopic characteristics in the formation gases. Most notably, the Devonian and Mannville Group gases are isotopically heavier ($\delta^{13}C_{1(PDB)} \approx -64$ ‰ and $\delta^{13}C_{2(PDB)} \approx -27$ ‰) than the Colorado Group formation gases ($\delta^{13}C_{1(PDB)} \approx -68$ ‰ and $\delta^{13}C_{2(PDB)} \approx -36$ ‰). These isotopic fingerprints enable the tracing of the source(s) of migrating gas as addressed in the next chapter.

4. MIGRATING GAS

4.1 Isotopic Signature

The carbon and hydrogen isotope compositions of the "leaking" well samples (migrating gases and producing formation gases) are listed in Appendix 2. The isotopic signatures of the surface casing and soil migration gases are summarized in Figure 4.1.

All of the soil migration and most of the surface casing gases are marked by exceptionally ^{13}C-depleted methane ($\delta^{13}C_{1(PDB)} \approx -69$ ‰), ethane ($\delta^{13}C_{2(PDB)} \approx -41$ ‰) and carbon dioxide ($\delta^{13}CO_{2(PDB)} \approx -16$ ‰) (Figure 4.1). Surface casing samples analyzed in 1988 as part of an unpublished Husky Oil Operations Limited study possessed the same isotopic composition ($\delta^{13}C_{1(PDB)} \approx -66$ ‰ and $\delta^{13}C_{2(PDB)} \approx -42$ ‰). The isotopic signature of these well-associated migrating gases is significantly different from those of the Devonian and Mannville Group solution gases ($\delta^{13}C_{1(PDB)} \approx -64$ ‰, $\delta^{13}C_{2(PDB)} \approx -27$ ‰ and $\delta^{13}CO_{2(PDB)} \approx -8$ ‰) (Figure 4.2). Methane, ethane and carbon dioxide with similar $\delta^{13}C$ values are, however, observed in the shallower Colorado Group gases (Figure 4.2). Of these near-surface strata, the isotope ratios of the Second White Speckled Shale gas ($\delta^{13}C_{1(PDB)} \approx -71$ ‰, $\delta^{13}C_{2(PDB)} \approx -39$ ‰ and $\delta^{13}CO_{2(PDB)} \approx -15$ ‰) and the "shallow" formation gas ($\delta^{13}C_{1(PDB)} \approx -70$ ‰, $\delta^{13}C_{2(PDB)} \approx -40$ ‰ and $\delta^{13}CO_{2(PDB)} \approx -12$ ‰) most closely match the isotopic fingerprint of the gas migrating from wells in the Lloydminster area. (The "shallow" horizon referred to is a zone somewhere above the Second White Speckled Shale that was perforated in the 9-6-55-6 W4M well. The exact formation sampled is unclear.) Figure 4.2 shows a trend of decreasing ^{13}C-content (with the exception of the propane and butane components) from depth toward surface so it is probable that the components of the uppermost gases, namely the First White Speckled Shale, the Lea Park and the Belly River Formation gases, are also depleted in ^{13}C. Unfortunately, no samples have clearly been obtained from any of these horizons. Even so, the trend of ^{13}C-enrichment with



* bubbles (soil migration gas)

\+ typical vent gas ($\delta^{13}C_2$ (PDB) ≈ -41 ‰)

x atypical vent gas ($\delta^{13}C_2$ (PDB) ≠ -41 ‰)

? It is uncertain whether these are "true" surface casing vent samples.

Figure 4.1. Summary of the carbon isotope composition of surface casing and soil migration gases of the Lindbergh area.

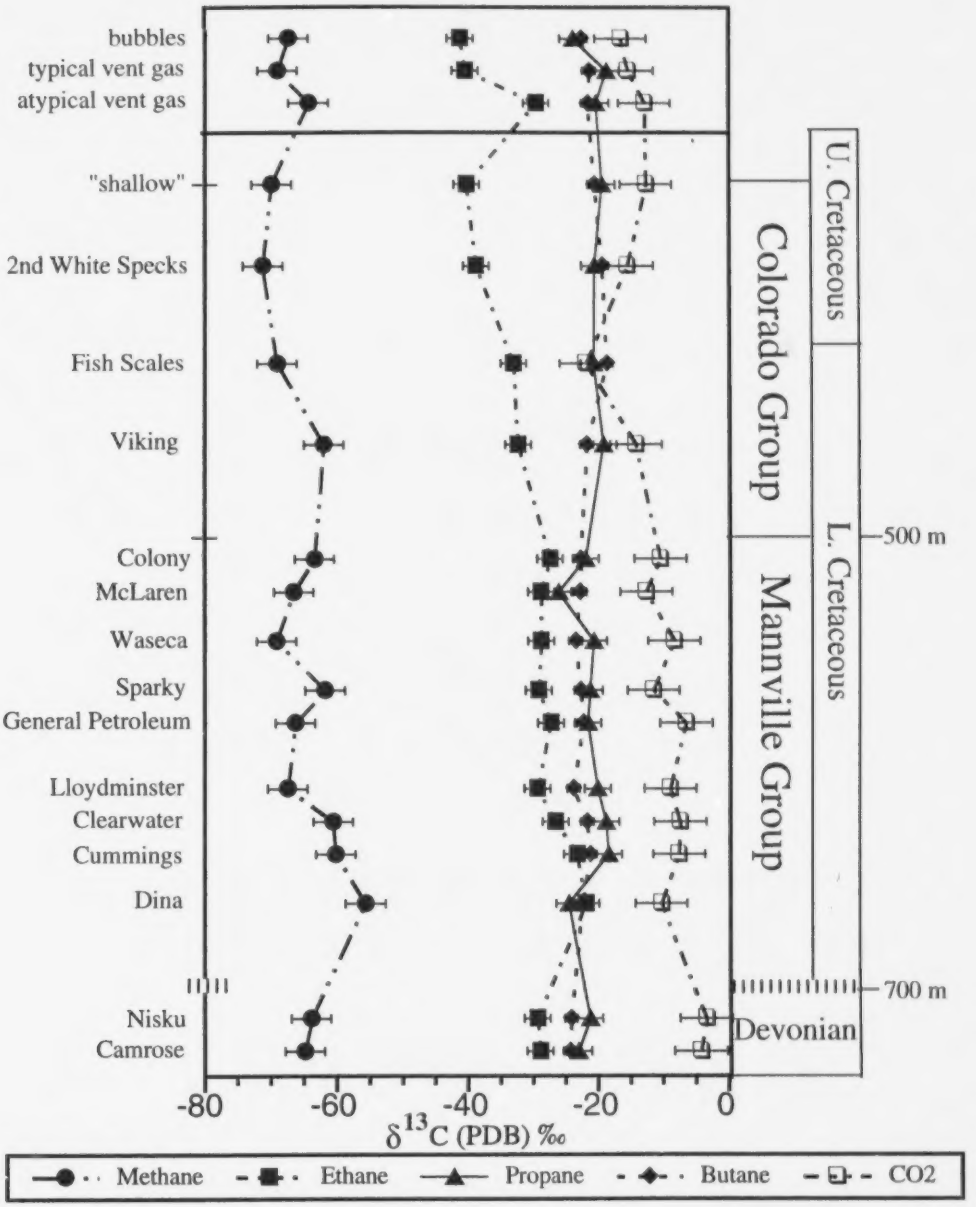


Figure 4.2. Comparison of the carbon isotope composition of migrating and solution gases of the Lindbergh region. The migrating gas samples have been separated into soil migration gases (bubbles), surface casing vent gases possessing ethane of low $\delta^{13}C$ value (typical vent gas) and surface casing vent gases which are relatively enriched in ^{13}C (atypical vent gas).

depth and the "shallow" formation gas signature reveal that the gas bubbles and most of the surface casing gases appear to originate from the shallow Upper Cretaceous Colorado or Montana Group strata.

A few of the surface casing gases are not marked with such isotopically light components (Figure 4.1). Unlike the more typical wellbore migration gases, the greater $^{13}C/^{12}C$ ratios of the constituents of these surface casing gases ($\delta^{13}C_{1(PDB)} \approx -64$ ‰, $\delta^{13}C_{2(PDB)} \approx -29$ ‰ and $\delta^{13}CO_{2(PDB)} \approx -13$ ‰) are more like those of the deeper Devonian and Mannville Group gases than those of the shallow Colorado Group horizons (Figure 4.2). The origin of these gas leaks, therefore, seems to be the Mannville strata from which the wells produce.

The soil migration gas samples possess an isotopic fingerprint like those of the gases from many of the sampled surface casing vents, but the methane component of the bubbles is slightly heavier whereas the carbon dioxide fraction is slightly more depleted in ^{13}C (Figures 4.1 and 4.3). The change in $\delta^{13}C$ values is indicative of the near-surface oxidation of the hydrocarbons. As bacteria preferentially utilize ^{12}C, the microbial oxidation of methane enriches the residual methane in ^{13}C and produces ^{12}C-rich carbon dioxide (Coleman *et al.*, 1981; James and Burns, 1984; Balabane *et al.*, 1987; Grossman *et al.*, 1989; Drimmie *et al.*, 1991).

4.2 Source of Migrating Gas

The gas migration study was well-specific and restricted to the Lindbergh field with the exception of three nearby wells (6-8-49-6 W4M, 11-3-50-4 W4M and 3-16-51-9 W4M). The studied problem wells tended to be producing from the Colony, Sparky and Cummings Formations. The isotopic signatures of the migrating gases associated with the wells need not match those of the producing horizons.

In many problem wells (6A-17-55-4 W4M, 4D2-18-55-5 W4M, 16-4-55-6 W4M, 1A-5-55-6 W4M and 9-6-55-6 W4M), the isotopic composition of the producing

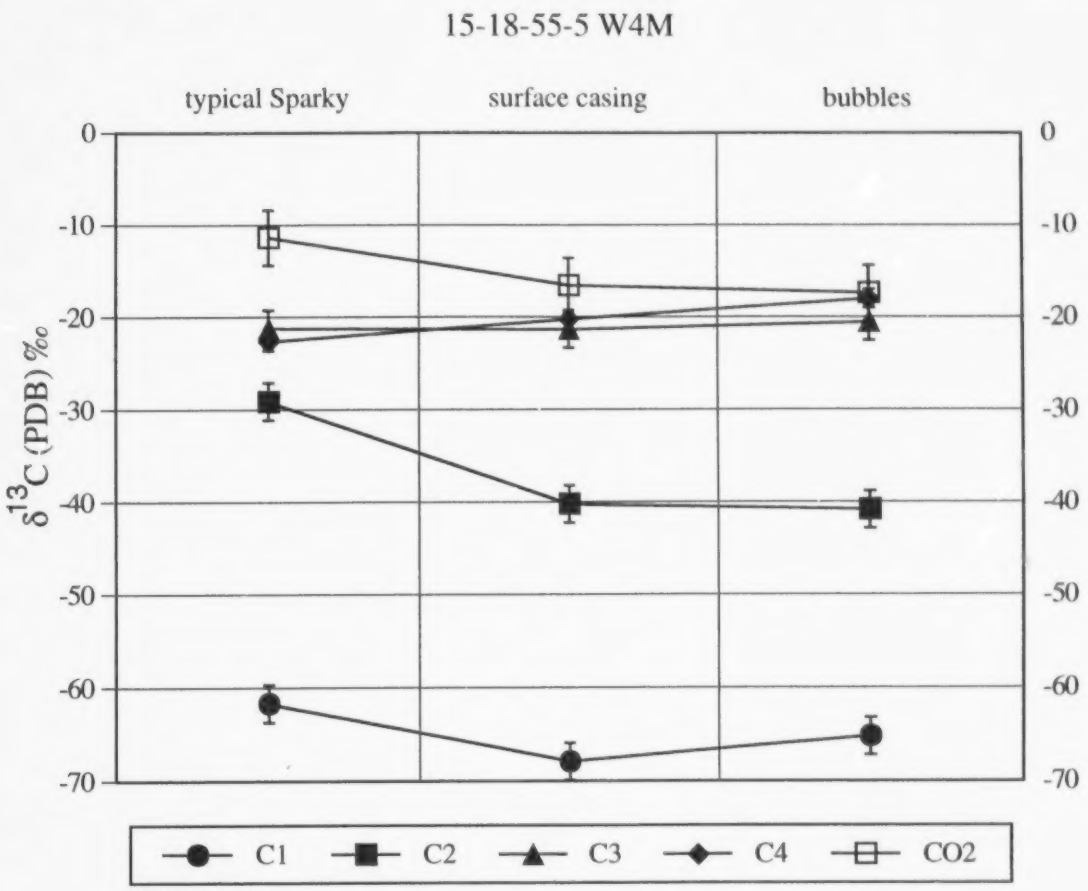


Figure 4.3. Comparison of the carbon isotope composition of surface casing and soil migration gases. The gas migrating to surface outside the well casing (up to 25 m away) at 15-18-55-5 W4M contains C_1 which is slightly richer in ^{13}C than the vent gas and CO_2 which is slightly richer in ^{12}C. Neither of the migrating gas forms observed around the well possess an isotopic signature like that expected of the lease's production horizon (Sparky).

horizon gas is typical of the completion horizon, yet the migrating gas associated with the well has a different fingerprint (Figure 4.4). Surface casing gases from 11-3-50-4 W4M, 3-16-51-9 W4M, 15-18-55-5 W4M and 1A-3-56-5 W4M possess ^{13}C-depleted ethane ($\delta^{13}C_{2(PDB)} \approx -41$ ‰) (Figure 4.1). Though no producing horizon gases were analyzed from these wells, the fingerprint of the migrating gas at these sites is quite different from the Mannville Group completion horizon signatures listed in Figure 3.1. These situations reveal that gas leakage does not originate from the deep producing horizons. This, like the similarity between the migrating gas and Colorado Group gas isotopic compositions, indicates that the source of migrating gas observed around the Lindbergh area wells is the shallower Upper Cretaceous zones.

The argument of the shallow strata being the source of the migrating gas observed around wellbores in the Lindbergh region of Alberta is further supported by the isotope data of wells 4D2-18-55-5 W4M, 9-6-55-6 W4M, 16-8-55-6 W4M and 16A-8-55-6 W4M. Remedial efforts to eliminate gas leakage from 4D2-18-55-5 W4M and 9-6-55-6 W4M included performing cement squeezes up the wellbores. Production horizon and surface casing samples were collected with each perforation. An isotopic match between the production and surface casing gases was achieved when the Second White Speckled Shale was perforated in 4D2-18-55-5 W4M and when a "shallow" formation somewhere above the Second White Speckled Shale was tapped in 9-6-55-6 W4M (Figure 4.5). Wells 16-8-55-6 W4M and 16A-8-55-6 W4M produce from the Second White Speckled Shale, and the isotopic signature of the migrating gases associated with these wells is like that of the Colorado Group formation from which they produce (Figure 4.6). The origin of the gas leaks of these wells, thus, seems to be the Second White Speckled Shale and a shallower formation of the Colorado Group.

Migrating gas from a few of the problem wells did not contain ethane with a $\delta^{13}C$ value of -41 ‰ (5-16-55-4 W4M, 1A-20-55-4 W4M, 11A-29-55-4 W4M, 4-9-55-5 W4M, 14A-26-55-6 W4M and 7A-3-56-5 W4M) (Figure 4.1). The ^{13}C content of the

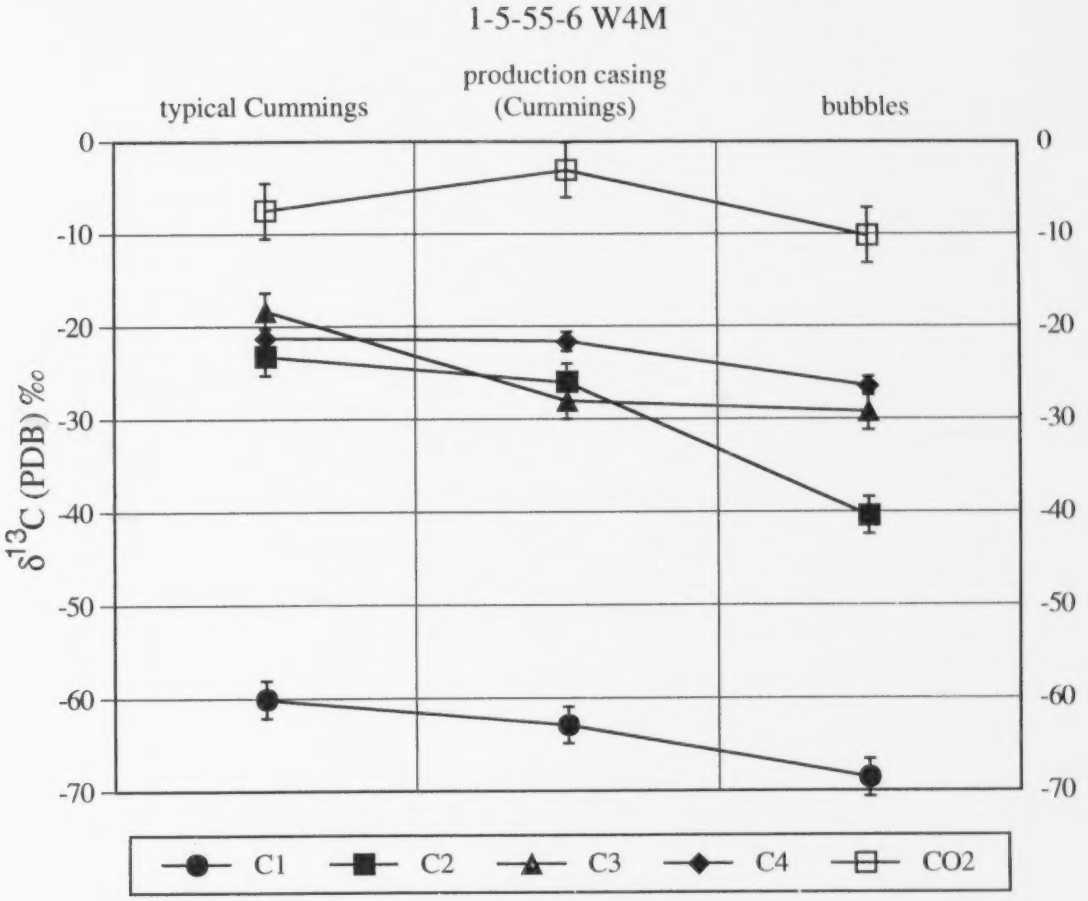
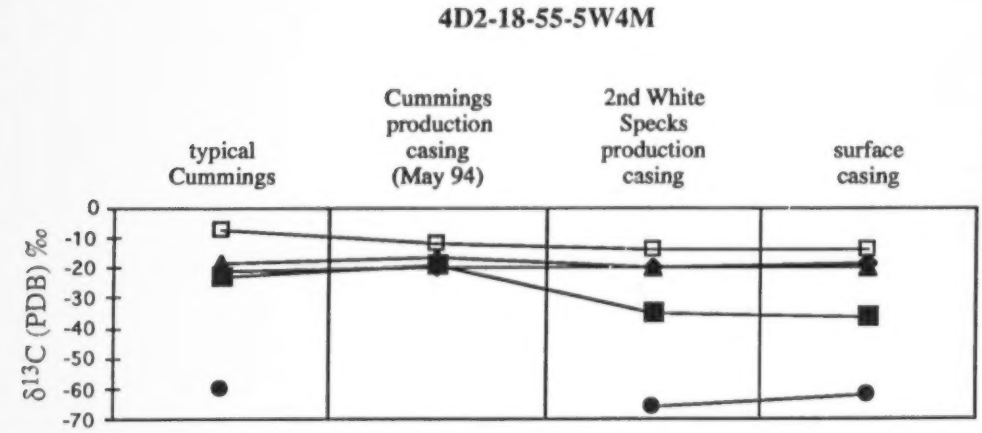


Figure 4.4. Example where the migrating gas observed around the wellbore is not the solution gas from depth. The situation at 1-5-55-6 W4M is typical of the studied problem wells. The production casing gas is isotopically like the produced solution gas (Cummings), but the migrating gas signature is different.

a)



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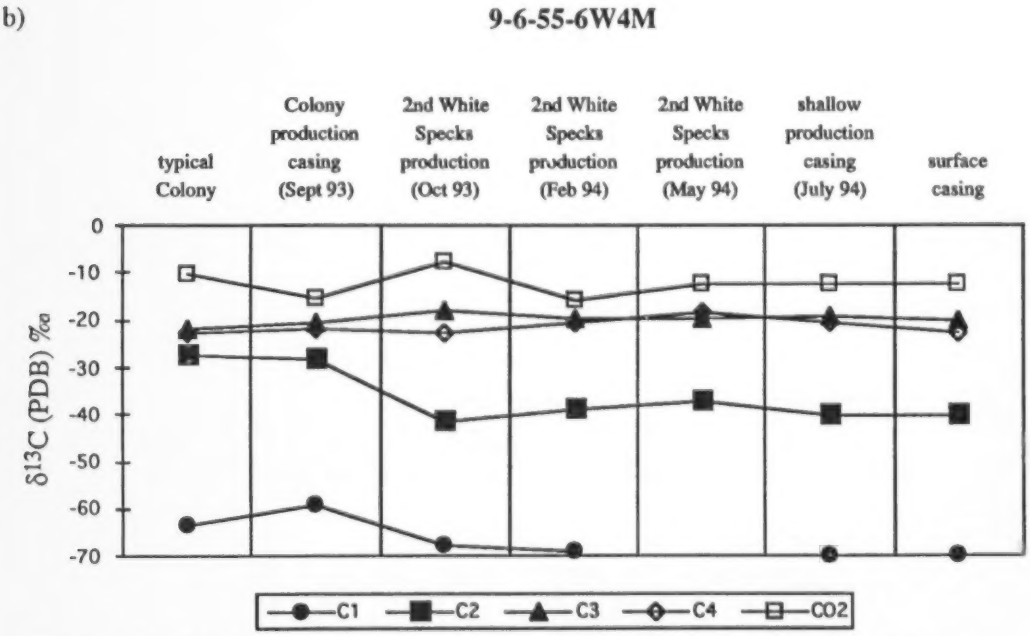

Figure 4.5. Comparison of the isotope composition of surface casing vent gas and various formation gases associated with a given lease. (a) 4D2-18-55-5 W4M is completed in the Cummings Formation. Analyses of gases from perforations throughout the wellbore indicate that the migrating gas is originating from the Second White Speckled Formation at this site. (b) 9-6-55-6 W4M is completed in the Colony Formation. The migrating gas signature at this site is like that of a "shallow" formation (above the Second White Speckled Shale) gas, indicating that the source of migrating gas is this "shallow" strata. (The standard deviation of the δ values is smaller than the symbol size.)

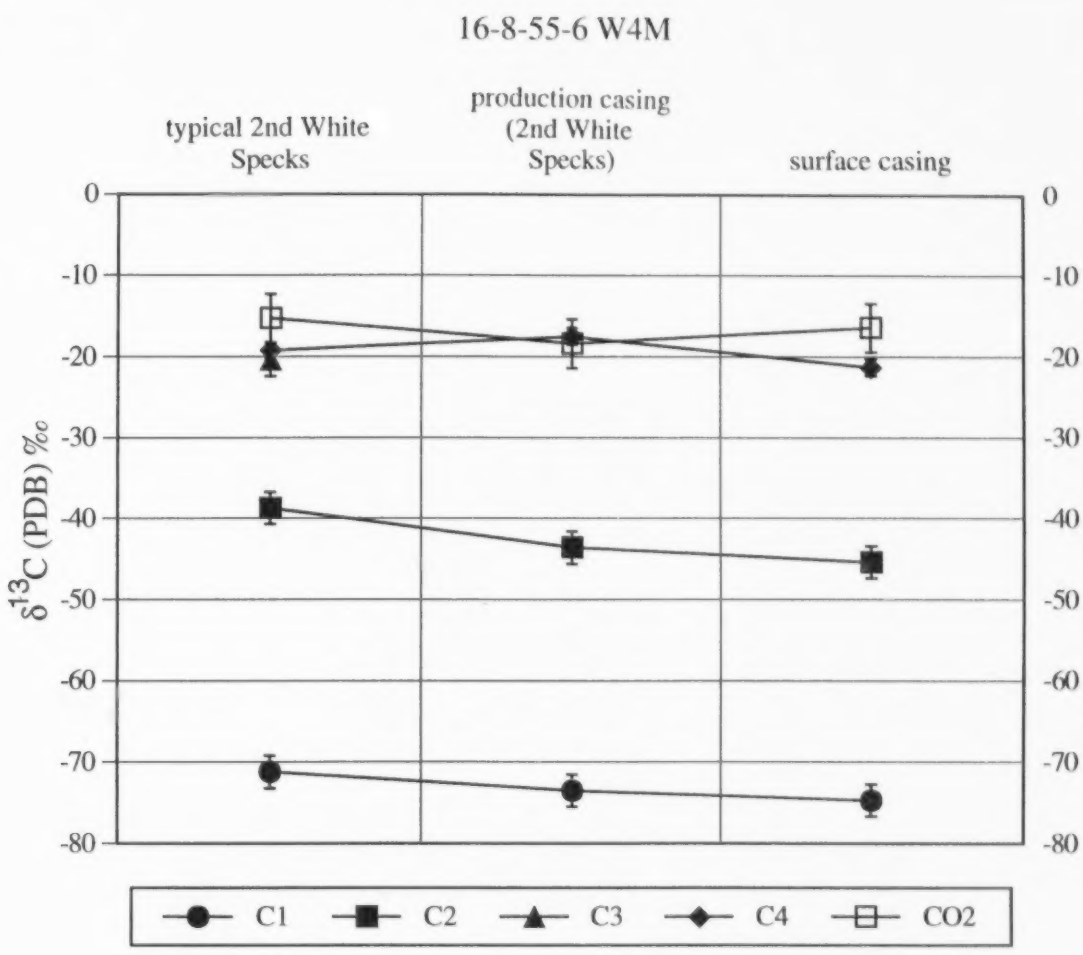

Figure 4.6 Comparison of the carbon isotope composition of surface and production casing gases from a well completed in the Second White Speckled Shale (16-18-55-6 W4M).

methane and ethane components of these gas samples is more variable than that of the migrating gas tagged with -41 ‰ ethane ($\delta^{13}C_{1(PDB)} \approx$ -72 to -58 ‰ and $\delta^{13}C_{2(PDB)} \approx$ -34 to -17 ‰). Production casing samples were obtained from only one of these wells (7A-3-56-5 W4M). At this site, the isotope composition of the leaking gas is similar to that of the Cummings Formation, the horizon from which the well produces (Figure 4.7). Although no production casing samples were analyzed, the isotope content of the migrating gas associated with the other wells lacking the -41 ‰ ethane tends to reflect that which was deemed typical of their production horizons. Therefore, the surface casing gases of these problem wells appear to be migrating from the Mannville Group formations in which the wells are completed.

Two wells whose surface casing gas is not marked with ethane of exceptionally low $\delta^{13}C$ value are not categorized as cases where the leakage is originating from the deep Mannville Group strata (6-8-49-6 W4M and 8A-24-55-5 W4M). Though migrating gas may be originating from depth at these sites, it is uncertain whether the collected gases are indeed "true" surface casing migration gas samples. 6-8-49-6 W4M is a capped well. That is, caps have been welded over the well's surface and production casings (Figure 4.8a). Though this is definitely a problem well (pressure is observed in the surface casing), the sample may be of gas migrating around the wellbore and into the surface casing, or it may be leaking from the production casing if the underlying cap is imperfect. The upper portions of the production casing of 8A-24-55-5 W4M are weak (Figure 4.8b). When the surface casing vent is shut, soil gas migration bubbles appear around the well. When the vent is opened, gas bubbling around the well ceases. The isotopic composition of the surface casing gas of this well is typical of Mannville Group gas, hinting that the collected sample was production gas and that the pressure observed in the outer casing is due to production casing failure. Unfortunately, no soil migration gas samples were obtained from the site to confirm this.

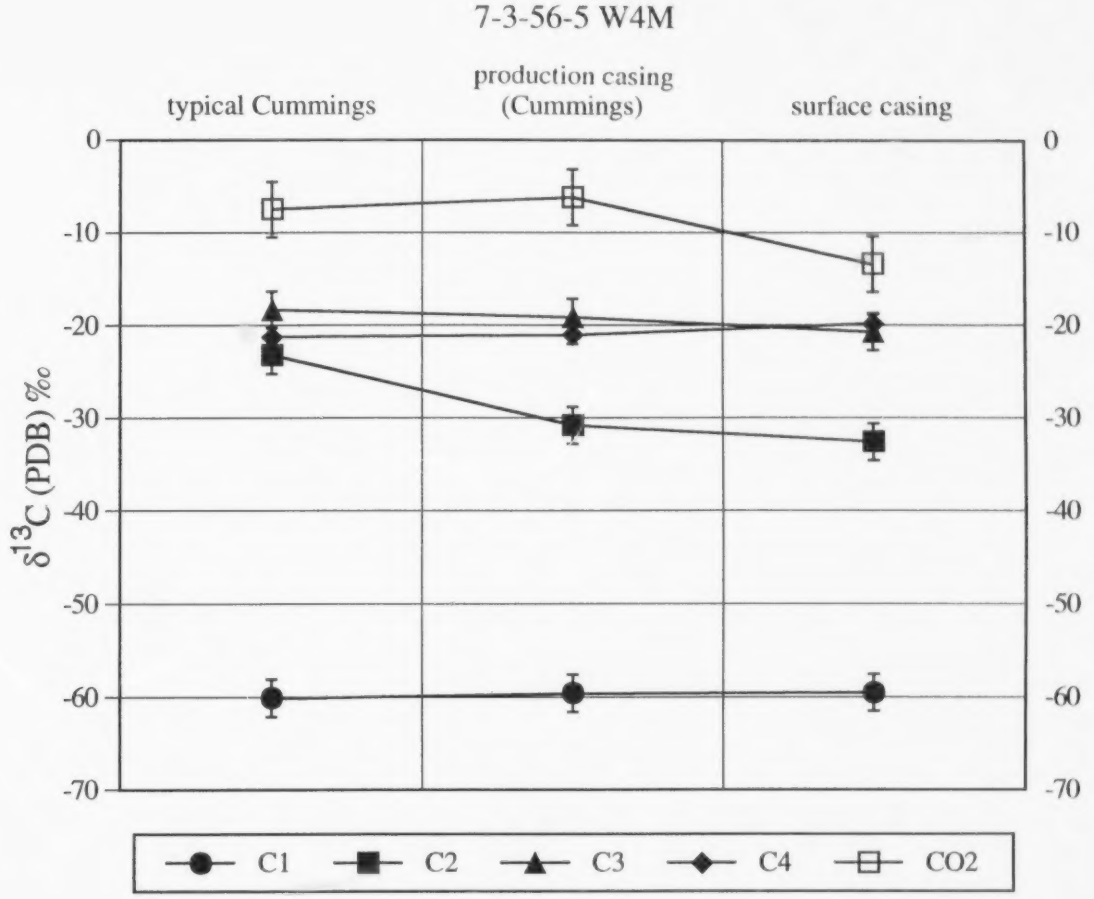

Figure 4.7. Example where the carbon isotope composition of the surface casing gas lacks -41 ‰ ethane and is similar to that of the Mannville formation from which the well produces (7-3-56-5 W4M).

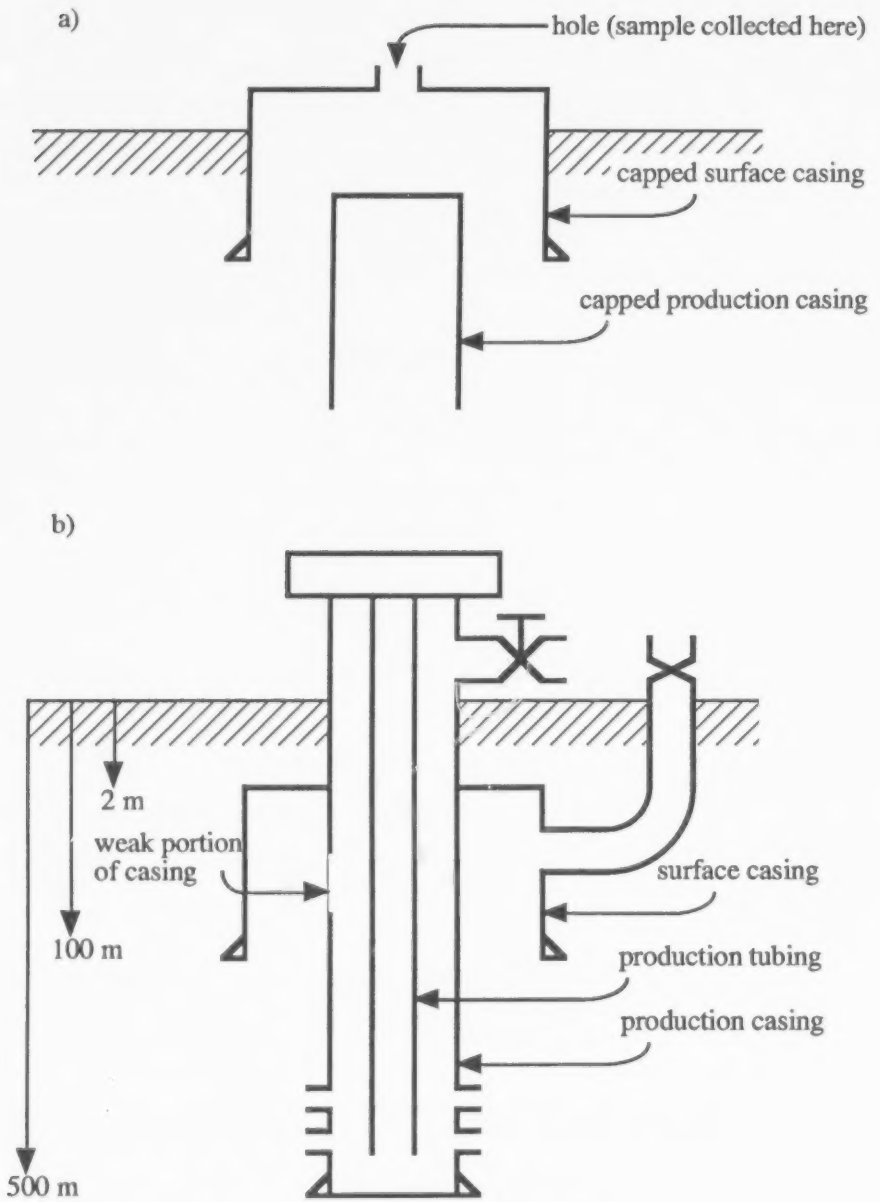

Figure 4.8. Schematics of leases where the gases collected from surface casing vents may not be "true" representatives of well-associated migrating gas. (a) 6-8-49-6 W4M is a capped well. (b) 8A-24-55-5 W4M has imperfect production casing.

4.3 Origin of ^{13}C-depleted Ethane

Early data from Amoco Canada Petroleum's 16-4-55-6 W4M well suggested that gas dissolved in stagnant formation water may be the source of the observed -41 ‰ ethane signature. The soil migration gas observed around this well is marked by the ^{13}C-depleted ethane typical of the migrating gas associated with wells in the Lindbergh region. The initial Sparky production horizon samples (April and May, 1994) were also characterized by this ethane (Figure 4.9a). On those collection dates, however, there was very little pressure in the Sparky Formation at this lease, and the efforts exhausted to build pressure failed. Such conditions are typically indicative of formation fluid in the well. These early production horizon samples were "old" as the hydrostatic head of the fluid prevented new formation gas from entering the well. The water was then blown out of the well, and new production casing samples were collected (December, 1994). These later production horizon samples possessed a markedly different isotopic composition, that typical of Sparky gas (Figure 4.9a). Therefore, the -41 ‰ ethane observed in the early production casing samples of 16-4-55-6 W4M was not a reflection of the completion horizon signature but rather a component of the stagnant gas. This initiated an investigation of stagnant formation water as the source of the -41 ‰ ethane signature. Three other fluid-filled wells were tested (2A-14-56-7 W4M, 1A-6CW-56-6 W4M and 5A-6CW-56-6 W4M). None of the formation gases from these wells possessed the ^{13}C-depleted ethane (Figure 4.9b). As the isotopic signatures of these stagnant samples matched those thought typical of the formations from which they produce (Figure 4.9b), stagnant formation water is not the cause of the -41 ‰ ethane. The occurrence of the signature in the early samples of 16-4-55-6 W4M was site-specific.

The origin of the -41 ‰ ethane observed in the majority of the surface casing and soil migration gas samples is unclear. The ^{13}C content of the propane and butane components discount mild thermogenesis or microbial degradation as the cause of the fingerprint (see Chapter 3.2). Similarly, any physical diffusion mechanism which could

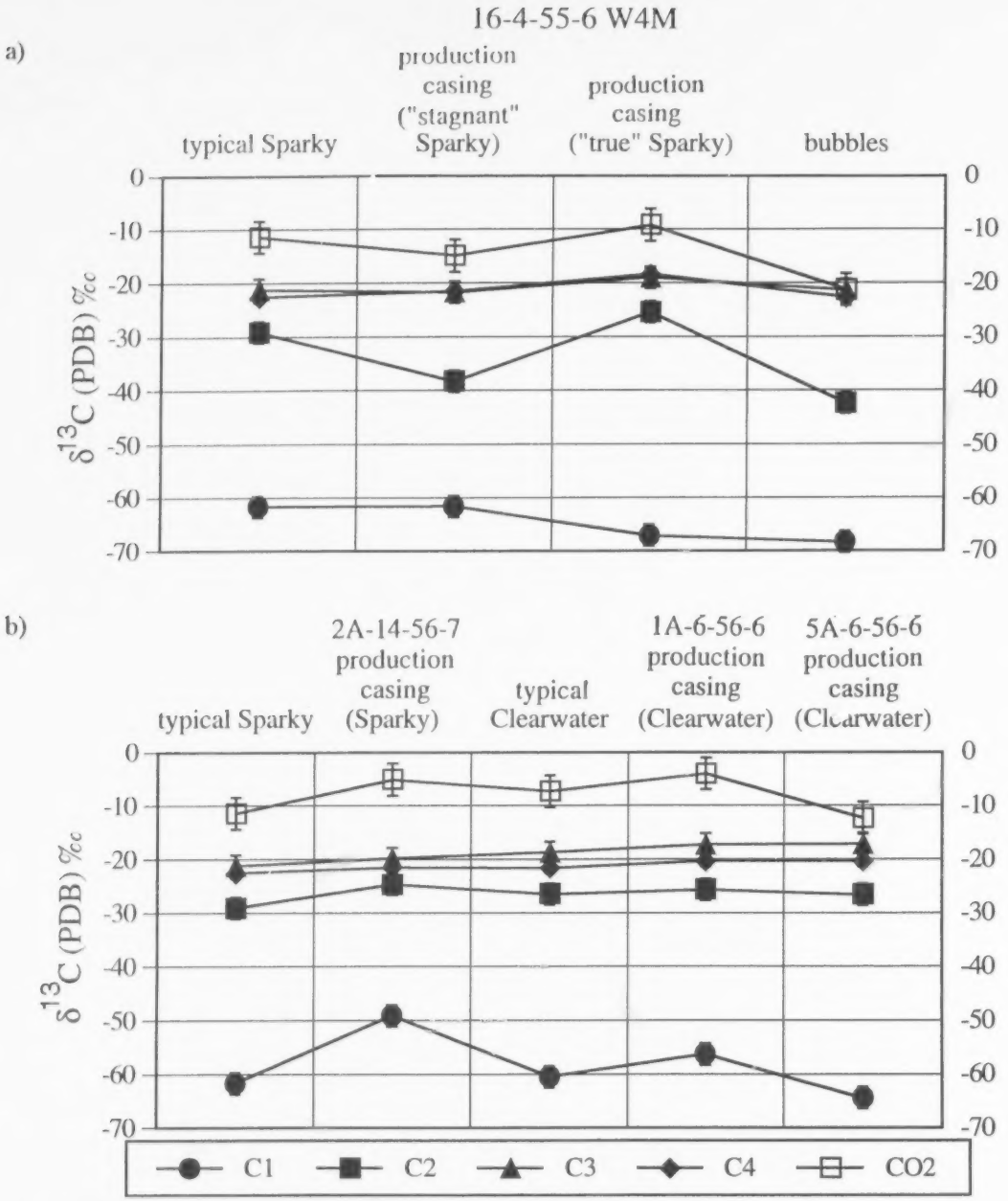

Figure 4.9. Investigation of stagnant formation water as the source of ethane with the $\delta^{13}C$ value of -41 ‰. (a) Early production casing samples from 16-4-55-6 W4M were stagnant and possessed the ^{13}C-depleted ethane typical of migrating gas. (b) None of the other tested stagnant well gases contained the unique ^{13}C-depleted ethane.

cause the ^{13}C-depletion in ethane would partition the ^{13}C content of the propane and butane fraction in the same manner. Perhaps the extremely ^{13}C-depleted ethane is derived from bacterial production of ethane. The accompanying exceptionally ^{12}C-rich methane component of the gases supports a bacteriogenic origin of the ethane.

4.4 Field Confirmation of the Source of Migrating Gas

The source of migrating gas from wells in the Lindbergh heavy oil field is, in most instances, the shallow Colorado Group strata. Recently, operators have achieved much better success in eliminating or reducing gas leakage from wells by focusing their remedial efforts on the White Speckled Shales (Halliburton Energy Services, 1995).

Amoco Canada Petroleum and Husky Oil have begun performing cement squeezes and Halliburton hydro-jet workovers on some of their problem wells. (Cement squeezes are designed to place cement at pressures below the formation fracture pressure (Halliburton Energy Services, 1995). Often more than one squeeze is required to intercept the migrating gas channel. The hydro-jet technique involves jetting 360° in a horizontal plane to ensure the interception of any migration channels between the borehole and the casing. The hydraulic fracturing allows for proper cement placement in the plane (Halliburton Energy Services, 1995).) The companies' efforts are mainly directed at the calcified shale below the top of the First White Speckled Formation. Workovers targeted at this shallow zone have been successful, whereas workovers performed below the Fish Scales Formation have been much less successful at controlling gas leakage. At 4D2-18-55-5 W4M, a circulating vent squeeze at the base of the Second White Speckled Shale did not reduce the rate of surface casing gas migration. A second squeeze using the hydro-jet technique performed in the First White Speckled Formation reduced the rate of gas leakage from 0.15 to 0.02 ft^3/hr (0.0043 to 0.0006 m^3/hr). Two similar workovers were carried out on 16-8-55-6 W4M, and here the rate of gas migration around wellbores dropped from 60 to 40 ft^3/hr (1.7 to 1.1 m^3/hr). Husky Oil reports

having completely eliminated gas leakage at 10 of its Lloydminster problem wells by targeting the First White Speckled Shale (Halliburton Energy Services, 1995).

The success achieved by Amoco Canada Petroleum and Husky Oil by concentrating their remedial efforts on the First White Speckled Shale indicates that the source of migrating gas from wells in the Lindbergh region is somewhere below this formation. The stable isotope data suggest that the source of most of the gas leakage is the Upper Cretaceous strata and not the underlying Mannville Group formations from which the wells produce. Other operators have reported success at mitigating the rates of gas migration from wells by working on the Second White Speckled Formation which is not contrary to these statements.

4.5 Summary

The majority of the migrating gas samples are tagged by ethane of exceptionally low $\delta^{13}C$ value ($\delta^{13}C_{2(PDB)} \approx -41$ ‰), a signature also present in the shallower Colorado Group gases. Often the surface casing migration gas fingerprint is very different from the producing Mannville horizon signature, but it is similar to that of the production casing gas in those wells completed or perforated in the Second White Speckled Formation. Therefore, an Upper Cretaceous zone gas with -41 ‰ ethane appears to be the dominant source of the migrating gas from wells in the Lindbergh field.

A few of the surface casing vent samples are not marked by the characteristic -41 ‰ ethane. The $^{13}C/^{12}C$ ratios of these migrating gases are like those of the Mannville Group gases which the wells produce from. In these rarer cases, the well-associated migrating gas seems to originate from the deeper formations.

The origin of the unique ethane carbon isotope composition typical of the gas migrating from wells in the Lloydminster region is unclear. The -41 ‰ $\delta^{13}C$ value may be derived from a rare biological process such as ethanogenesis.

Hydro-jet workovers targeted at the top of the First White Speckled Shale have

significantly reduced the rate of gas leakage at several wells in the Lloydminster region. The success of remedial efforts directed at the upper Colorado Group horizons confirms the Upper Cretaceous strata as the source of the migrating gas from wells in the region.

5. CONCLUSION

5.1 Conclusions

The problem of gas migration affects approximately half of the shallow producing wells in the Lloydminster area of Alberta and Saskatchewan. Regulation guidelines stipulate that leakage must be eliminated prior to well operation or abandonment. Prior to this study, various expensive engineering efforts aimed at the Mannville strata from which the wells produce have failed to stop migration. The lack of success at mitigation is a reflection of the limited understanding of the process, a problem that is alleviated by this work.

The main objective of this study was to determine the source of the migrating gas from wells in the Lloydminster area of Alberta and Saskatchewan. This task was accomplished using stable isotope analyses, and the main conclusions to be drawn from the study are as follows:

(1) The isotope content of the Mannville and Colorado Group gases reflect a predominant bacteriogenic origin. The gases associated with the Lloydminster heavy oils are variably mixed with small amounts of biodegraded thermogenic gas. The variability in the amount of the mixing and extent of biodegradation give rise to isotopic fingerprints which serve to uniquely characterize the various producing horizon gases. These distinctions enable the determination of the origin of gas leakage.

(2) The isotope composition of the majority of the migrating gas samples is similar to the signature of the upper Colorado Group gases. Recent remedial efforts focused on the shallow Upper Cretaceous strata have been successful at reducing and eliminating the problem. Though the source of most of the

surface casing and soil migration gases appears to be below surficial till in the upper Colorado (and perhaps the Montana) Group formations, a few of the surface casing gases possess $^{13}C/^{12}C$ ratios like those of the Mannville Group horizons from which the wells produce. Therefore, the migrating gas observed around these few wells appears to originate from the deeper strata.

(3) The "typical" migrating gas signature and the Second White Speckled Shale gas are tagged with ethane of exceptionally low ^{13}C content ($\delta^{13}C_{2(PDB)}$ = -41 ‰). The origin of such ^{13}C-depleted ethane is unclear. Mild thermogenesis, microbial degradation and diffusion cannot account for the signature observed in these gases. The isotopic composition of the ethane may be the result of a bacterial process. The dominance of ^{13}C-depleted methane and the trace content of higher hydrocarbons in these gases support ethanogenesis as the cause of the unique signature.

In summary, stable isotope analyses have proved to be a useful tool in determining the source of migrating gas from wells in the Lloydminster region. For the most part, remedial efforts should be directed at the near-surface Upper Cretaceous reservoirs.

5.2 Future Work

The well-associated gas migration study was limited. The problem leases studied were few in number (twenty) and restricted to the Lloydminster region. There is also a lack of information as to the effect(s) gas leakage is having on the groundwater and the soil surrounding the problem wells. For completeness, further investigation into these areas is needed. Specifically:

(1) Production casing gases of the First White Speckled, the Lea Park and the Belly River Formations should be analyzed to confirm the Upper Cretaceous zones as the source of the gas migrating from wells in the Lindbergh area. (Shallow formation gases from the Medicine Hat region of Alberta were recently analyzed. The Second White Speckled, Milk River and Medicine Hat Formation gases of this area all possessed the ^{13}C-depleted ethane which characterizes the migration gas observed around wellbores in the Lindbergh region.)

(2) Well-associated gas migration samples should be obtained throughout and outside of the Lloydminster region to determine the extent of the unique -41 ‰ ethane fingerprint and whether the majority of gas leaks from problem wells of other locales also originate from shallow strata.

(3) Further investigation of the few Lindbergh wells indicating migration from depth is needed. Leakage originating from the Mannville strata is rare. Perhaps deep portions of the production casings of these wells are weak. Remedial efforts at these leases should concentrate on the producing horizons.

(4) The migration of methane from leaking gas wells into aquifers may be a problem in the Lloydminster area. Recent investigations into the presence of methane in shallow aquifers near two problem wells in the Lloydminster region show that leakage has not created methane plumes of hazardous concentration in the groundwaters (see Appendix 4). The yearlong study, however, was limited (two sites). Monitoring of the methane plumes at these and other research sites should be continued to determine any trends of methane transport and to further the understanding of the effects of gas

leakage from wells on the region's aquifers.

Not withstanding the above, the gas migration study was successful as it illustrated that the source of gas leakage from wells in the vicinity of the City of Lloydminster is the shallow horizons.

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APPENDIX 1

List of Symbols and Glossary of Terms

1.1 List of Symbols

C_1	methane
C_2	ethane
C_{2+}	hydrocarbons higher than and including ethane
C_3	propane
C_4	butane
D	deuterium
DIC	dissolved inorganic carbon
ppt	part per thousand
PDB	Peedee Formation Belemnite standard
SMOW	Standard Mean Ocean Water standard
δ	delta (measure of isotopic abundance relative to a standard)
‰	per mil (parts per thousand)

1.2 Glossary of Terms

annulus The space left inside casing and outside any tubing strings inside that casing.

associated gas Gas which is associated with petroleum or oil.

bacteriogenic gas Natural gas produced by bacterial decay.

biodegraded gas Residual gas remaining after bacteria have consumed portions of a gas reservoir.

bubbles Soil migration gas.

casing Heavy metal pipe lowered into a borehole during or after drilling and cemented in place.

cement squeezes The forcing of cement slurry into a borehole at pressures below the formation fracture pressure in order to recement a channeled area behind the casing or to close off perforations.

completion horizon The formation from which the well produces.

dual completed well A well which produces from two horizons.

dry gas Gas which is predominantly methane (minor traces of higher hydrocarbons).

fractionation Processes which cause differences in the isotope compositions of different phases and compounds.

gas migration The leakage of gas toward the earth's surface along disturbed bores of oil and gas wells or from open hole abandonments.

heavy Relatively enriched in the heavier isotope (more positive δ values).

hydro-jet workover Jetting 360° in a horizontal plane and filling the fractured plane with cement.

leaking well A well with the problem of gas migration.

light Relatively depleted in the heavier isotope (more negative δ values).

non-associated gas Gas which is not associated with petroleum or oil.

primary gas Natural gas generated from a single source of organic material.

production casing The innermost casing string of a well. Production fluids enter the production casing, usually through perforations.

production horizon Rock stratum of an oil field that will produce petroleum or gas when penetrated by a well.

production tubing Small-diameter removal pipe which extends from the wellhead through the production casing and ends in the proximity of the perforations in the producing zone.

secondary gas Gas which has been mixed or altered and no longer represents a single,

original gas.

single completion well A well which produces from only one formation.

soil migration gas Migrating gas observed around wellbores which is released directly to the atmosphere outside the production casing of a well.

solution gas Gas which is associated with heavy oil.

sound well A well which does not display any evidence of gas migration.

surface casing The outermost casing string which usually extends from surface down to below the deepest potable aquifer. Its purpose is to protect potable water from contamination during drilling.

surface casing migration gas Gas which migrates up between the production and surface casings and is detectable as a pressure buildup in the surface casing.

thermogenic gas Natural gas produced by the thermochemical degradation of organic matter

wet gas Gas with elevated concentrations of higher hydrocarbons.

APPENDIX 2

Gas Well Isotope Data of the Lloydminster Region

Company : A. = Amoco Canada Petroleum Company Limited

H. = Husky Oil Operations Limited

T. = Transwest Gas Systems Limited

PCP = PanCanadian Petroleum Limited

E. = Elan Energy Incorporated

These companies often have partners at the listed properties, and the major partner and operator is given.

Region : major oil field well lies in

Well : Legal subdivision - Section - Township - Range

A given well may have several samples of the same date. Those of the same date are not repeat analyses, but rather duplicate samples.

Sample type : tubing production = formation gas sample where the gas came up the inside of the tubing

production casing = formation gas sample where the gas came up outside of the tubing (between the tubing and the casing)

surface casing vent = surface casing migration gas sample

"surface casing vent?" = unclear whether these samples are "true" surface casing migration gas samples (A cap is welded over the surface casing

and the underlying production casing is also capped at 6-8-49-6 W4M, and shallow portions of the production casing of 8A-24-55-5 W4M are known to be weak.)

well culvert edge = soil migration gas sample collected within feet of the outermost well casing (collected from water or mud bubbles as indicated)

South East corner = soil migration gas sample collected ~ 25 m from the wellhead

surface in well crib = soil migration gas sample collected within the well's outermost casing

Formation : Table A2.1 has the sampled production horizons arranged by stratigraphic depth. The formations listed for migrating gas samples (Table A2.2) are the horizons from which the wells produce.

Nisku and Camrose are Devonian strata.

"Sparky" - The 16-4-55-6 W4M well produced from the Sparky Formation. The early samples were of low source pressure and the formation would not pressure up, indicating that formation fluid was in the well. These gas samples were "stagnant" as the hydrostatic head of the fluid prevented new formation gas from coming in. The water was blown out of the well to allow Sparky gas to enter. The later production casing samples from this well are thus inferred to be the Sparky gas typical of that well.

"Shallow" - These 9-6-55-6 W4M tubing production samples were obtained from perforations at a depth above the Second White Speckled

Shale. The exact formation sampled is not clear.

Date : sampling date

Data : The carbon and hydrogen isotopic data are listed in units of ‰ relative to PDB and SMOW, respectively.

C_1 = methane

C_2 = ethane

C_3 = propane

C_4 = butane

P : source pressure

H_2S : H_2S concentration

Note: * = sample was > 50 % air (Sample 11-2-55-6 W4M of the Cummings Formation was diluted with air to determine the effect of concentration on the isotopic results. The diluted sample (62 % air) C_1, C_2, C_3 and C_4 $\delta^{13}C$ values were ~ 4 ‰ higher than their concentrated sample (5 % air) counterparts. The ^{13}C content of the CO_2 component and the δD values were not affected by dilution.)

! = dual completed well (the second producing formation is also given)

+ = surface casing was left open (venting) for 3 weeks (15-18-55-5 W4M)

? = The top of the surface casing is ~ 6 ft below the surface at this site (8A-24-55-5 W4M). A portion of the production casing immediately above the surface casing is thought to be weak. When this well's surface casing is left open, a small gas flow out the vent occurs. When the surface casing vent is closed, bubbles of gas are observed in the water pools around the wellbore.

CAP = Theoretically there should be no pressure on this well (6-8-49-6 W4M) as both the production and surface casings are capped.

D&A = drilled and abandoned (These wells were completed with surface casings but not production casings. Electric logs revealed poor formation so no money or time was wasted on such pipe. The holes were simply filled with cement.)

OBS = observation well (A6-7-51-24 W3M)

STAG = stagnant water well (The early production casing samples from Amoco Canada Petroleum's 16-4-55-6 W4M well were stagnant. The isotopic signature of the production gas when the well was liquid-loaded appeared to match that of migrating gas. The "true" production gas of the well, collected after the water was removed from the well, did not possess the migrating gas isotopic fingerprint. This initiated an investigation of stagnant formation water as the source of the migrating gas isotopic signature.)

Table A2.1 : $\delta^{13}C$ (PDB) and δD (SMOW) values (‰) of the hydrocarbon components of production gases of the Lloydminster region.

Company (Region)	Well	Sample Type	Formation	Date	C1 $\delta^{13}C$	C1 $\delta^{2}D$	C2 $\delta^{13}C$	C2 $\delta^{2}H$	C3 $\delta^{13}C$	C3 $\delta^{2}H$	C4 $\delta^{13}C$	C4 $\delta^{2}H$	CO_2 $\delta^{13}C$	P / H2S	Note
H.Tangle Flags	A6-7-51-24 W3M	production casing	2nd White Specks	94/08/10		-294	-30.6	-262	-18.7	-200	-14.8	-183	-13.0	1000 kPa; 0 ppm	*
H.Tangle Flags	A6-7-51-24 W3M	production casing	2nd White Specks	94/08/10	-73.2	-317	-33.8	-227	-19.3	-215	-20.9	-194		1000 kPa; 0 ppm	
H.Tangle Flags	A6-7-51-24 W3M	tubing production	2nd White Specks	94/10/20	-76.2	-309	-40.5	-194	-18.9	-200	-17.7	-220	-24.2	130 psi	OBS
H.Tangle Flags	A6-7-51-24 W3M	tubing production	2nd White Specks	94/10/20	-76.1	-313	-37.6	-194	-18.2	-177	-18.3	-193	-12.2	130 psi	OBS
H.Tangle Flags	6-18-51-24 W3M	production casing	2nd White Specks	94/08/10	-74.5	-277	-39.3	-173	-20.9	-224	-21.5	-204	-15.5	1000 kPa	I Colony
H.Tangle Flags	6-18-51-24 W3M	production casing	2nd White Specks	94/08/10	-74.8		-41.2		-19.2		-20.4		-11.7	1000 kPa	I Colony
H.Tangle Flags	6-18-51-24 W3M	production casing	2nd White Specks	94/06/10	-73.0	-323	-38.8	-204	-22.1	-184	-19.0	-224	-10.1	1000 kPa	I Colony
H.Tangle Flags	6-18-51-24 W3M	production casing	2nd White Specks	94/06/10	-74.6		-40.1		-17.3				-11.2	1000 kPa	
H.Tangle Flags	6-18-51-24 W3M	tubing production	2nd White Specks	94/10/20	-67.5	-313	-37.6	-168	-18.0	-206	-18.5	-196	-13.3	1000 kPa	
H.Tangle Flags	6-18-51-24 W3M	tubing production	2nd White Specks	94/10/20	-72.0	-289	-43.1	-175	-43.8	-143	-21.4	-203	-33.7	1000 kPa	
T.Fort Kent	5A-28-61-4 W4M	tubing production	Fish Scales	94/10/17	-68.1		-36.6		-23.1				-28.0	100 psi	
T.Fort Kent	5A-28-61-4 W4M	tubing production	Fish Scales	94/10/17	-67.8	-308	-34.7	-193	-19.7	-255	-18.7	-205	-28.2	100 psi	
T.Fort Kent	5A-28-61-4 W4M	tubing production	Fish Scales	94/10/17	-70.1	-393	-32.8	-160	-21.2	-206	-19.4	-197	-33.8	100 psi	
T.Fort Kent	5A-28-61-4 W4M	tubing production	Fish Scales	94/10/17	-70.0	-326	-29.6	-173	-20.0	-184	-18.0	-205	-30.9	100 psi	
T.Fort Kent	6-20-61-4 W4M	tubing production	Fish Scales	94/10/18					-17.4		-20.0		-14.2	200 psi	*
T.Fort Kent	6-20-61-4 W4M	tubing production	Fish Scales	94/10/18	-67.0	-334	-35.6	-217	-19.8	-228	-18.9	-238	-12.0	200 psi	
T.Fort Kent	6-20-61-4 W4M	tubing production	Fish Scales	94/10/18	-70.0	-330	-29.4	-190	-23.3	-466	-17.0	-284		200 psi	
T.Fort Kent	6-20-61-4 W4M	tubing production	Fish Scales	94/10/18	-70.0	-293	-31.9	-158	-19.4	-157	-17.3	-342		200 psi	
H.Wainwright	7B-14-45-7 W4M	tubing production	Viking	94/01/10	-61.9	-312	-32.2	-206	-19.0	-241	-21.6	-213	-14.0	trace	
H.Wainwright	A11C-5-45-4 W4M	tubing production	Colony	94/01/10	-65.1	-318	-27.5	-240		-193	-23.1	-210	-6.4	trace	
H.Wildmere	10D-32-47-4 W4M	production casing	Colony	94/03/25	-57.8	-301		-281	-22.0	-226	-24.3		-9.9		*
H.Wainwright	16D-18-46-6 W4M	tubing production	Colony	94/01/10	-62.3	-314	-27.4	-253		-296	-21.8	-332	-10.7	<1 ppm	
H.Big Gully	A14-5-50-24 W4M	tubing production	Colony	94/03/24	-67.9	-326	-29.1	-152	-23.9	-253	-22.3	-170	-6.1		
H.	6-18-51-24 W3M	tubing production	Colony	94/08/10	-71.1	-317	-27.4	-324	-19.2	-298	-19.9	-163	-26.5	0 kPa	I 2nd White Specks
H.	6-18-51-24 W3M	tubing production	Colony	94/08/10	-72.1		-27.0		-20.5		-22.1		-11.9	0 kPa	I 2nd White Specks
H.Big Gully	A12-1-50-25 W3M	tubing production	Colony	94/03/24		-294	-30.0	-159	-20.1	-180	-22.8	-183	-2.6		
A.Lindbergh	10-7-56-6 W4M	production casing	Colony	94/02/15	-59.6	-303	-21.5		-24.4	-212	-23.7	-204	-12.0		
H.Lloydminster	6C-27-42-2 W4M	production casing	McLaren	94/03/11	-61.7	-291	-29.0	-224	-25.9	-232	-21.5	-214	-14.1		
H.Lloydminster	16C-28-48-2 W4M	production casing	McLaren	94/03/11	-63.3	-265	-28.0	-230	-36.6	-213	-24.1	-241	-13.2		
H.Big Gully	3-3-50-25 W3M	production casing	McLaren	94/03/24	-66.3	-299	-29.3	-196	-26.1	-180	-23.3	-179	-13.5		
H.	2A6-7-51-24 W3M	production casing	McLaren	94/08/10	-69.9	-323	-28.0	-153	-18.4	-192	-22.6	-198	-9.0	1000 kPa	
H.	2A6-7-51-24 W3M	production casing	McLaren	94/08/10	-71.1	-320	-29.8	-179	-24.0	-234	-24.0	-256	-11.8	1000 kPa	
H.	A9-17-51-24 W3M	tubing production	McLaren	94/08/10	-68.9	-292	-28.0	-235	-18.8	-196	-21.0	-197	-10.4	900 kPa	
H.	A9-17-51-24 W3M	tubing production	McLaren	94/08/10	-72.0		-28.4		-22.0		-21.8		-12.4	900 kPa	
H.Lushburn	5-2-49-24 W3M	production casing	Waseca	94/03/24	-70.3	-300	-30.1	-296	-19.3	-291	-23.0	-225	-7.6		
H.Lushburn	D1-13-49-25 W3M	production casing	Waseca	94/03/24	-68.2	-356	-28.5	-237	-22.2	-276	-23.6	-249	-8.0		
H.Forest Bank	D6-13-49-25 W3M	production casing	Waseca	94/03/24	-68.7	-292	-26.5	-214	-20.3	-214	-23.8	-257	-9.0		
H.Wainwright	2D-19-46-6 W4M	tubing production	Sparky	94/01/10	-62.9	-321	-26.5	-226	-22.0	-218	-22.5	-284	-9.0	<1 ppm	
H.Devonia	11A-30-49-1 W4M	production casing	Sparky	94/03/11	-65.0	-299	-28.4	-206	-24.2	-230	-24.3	-197	-9.0		
H.Devonia	13A-30-49-1 W4M	production casing	Sparky	94/03/11	-63.6	-282	-26.7	-293	-23.2	-236	-23.0	-226	-11.2		
H.Lushburn	D2-13-49-25 W3M	production casing	Sparky	94/03/24	-65.9	-296	-27.9	-226	-19.0	-220	-23.8	-234	-10.5		
A.Lindbergh	7-29-55-4 W4M	production casing	Sparky	94/03/01	-60.7	-307	-29.4	-209	-20.5	-193	-19.9	-192	-5.4		
A.Lindbergh	2A-3-55-6 W4M	production casing	Sparky	94/04/20		-297		-122	-18.2	-149	-20.4	-200	-9.7		*
A.Lindbergh	2A-3-55-6 W4M	production casing	Sparky	94/04/20	-59.6	-323	-29.1	-58	-26.4	-175	-23.0	-216	-10.0		
A.St.Paul	13A-12SK-56-7 W4M	tubing production	Sparky	94/02/28	-60.7	-307	-29.1	-233	-21.5	-226	-21.7	-223	-9.8		
A.Lindbergh	2A-14-56-7 W4M	production casing	Sparky	94/10/04	-49.1	-334	-24.7		-19.8	-194	-21.5		-5.1	250 psi	STAG
PCP Wainwright B	4B-13-48-9 W4M	production casing	Sparky	94/04/04	-58.1	-291		-221	-17.1	-226	-25.6	-249			*
PCP Wainwright B	16D-13-48-9 W4M	production casing	Sparky	94/04/04	-61.4	-294	-23.5	-186	-22.8	-186	-25.5	-175	-26.2		
H.	10A-36-48-1 W4M	production casing	Gen.Petroleum	94/03/11	-64.3		-27.7	-199	-19.4	-197	-24.6	-181	-3.2		
H.	15A-36-48-1 W4M	production casing	Gen.Petroleum	94/03/11	-63.5	-291	-25.8	-186	-27.2	-218	-23.0	-224	-1.5		
H.Big Gully	A12-4-50-24 W4M	production casing	Gen.Petroleum	94/03/24	-66.0	-320	-28.3	-292	-19.8	-168	-19.4	-182	-10.5		

Company (Region)	Well	Sample Type	Formation	Date	C1 $\delta^{13}C$	C1 $\delta^{2}H$	C2 $\delta^{13}C$	C2 $\delta^{2}H$	C3 $\delta^{13}C$	C3 $\delta^{2}H$	C4 $\delta^{13}C$	C4 $\delta^{2}H$	CO2 $\delta^{13}C$	P / H2S	Note
H.	A13-7-51-24 W3M	production casing	Gen.Petroleum	94/08/10	-67.4	-298	-21.2	-184	-18.5	-158	-21.3	-164	-10.0	1ppm	
H.	A13-7-51-24 W3M	production casing	Gen.Petroleum	94/08/10	-70.8	-312	-32.5	-228	-20.2	-206	-21.9	-218	-10.8	1ppm	
H.Wildmere	12C-16-47-4 W4M	production casing	Lloydminster	94/03/25	-65.7	-300	-32.1	-212	-21.5	-280	-24.0	-195	-6.7		
H.Wildmere	13C-16-47-4 W4M	production casing	Lloydminster	94/03/25	-63.5	-265	-29.6	-148	-21.0	-215		-188	-5.8		
H.Big Gully	A9-5-50-24 W3M	tubing production	Lloydminster	94/03/24	-67.9	-311	-29.3	-211	-19.6	-188	-24.6	-152	-12.7		
H.	A7-7-51-24 W3M	production casing	Lloydminster	94/08/10	-69.5	-293	-26.7	-202	-16.0	-178	-22.0	-154	-9.8	0.5 ppm	
H.	A7-7-51-24 W3M	production casing	Lloydminster	94/08/10	-71.0	-309	-27.7	-204	-23.2	-242	-26.1	-251	-9.8	0.5 ppm	
H.	A2-19-51-24 W3M	production casing	Lloydminster	94/08/10	-69.5	-322	-28.1	-287	-19.2	-197	-22.4	-213	-9.0	0.5 ppm	
H.	A2-19-51-24 W3M	production casing	Lloydminster	94/08/10	-69.8		-28.0		-17.8		-21.5		-8.9	0.5 ppm	
A.Lindbergh	1C-29CW-55-6 W4M	production casing	Clearwater	94/02/22		-266			-19.6	-212	-23.3	-213	-7.8		*
A.Lindbergh	11C-32-55-6 W4M	production casing	Clearwater	94/02/22	-60.8	-322	-27.1		-21.0	-221	-22.3	-245	-5.2		
A.Lindbergh	1A-6CW-56-6 W4M	production casing	Clearwater	94/10/04	-56.3	-331	-25.7	-225	-17.2	-206	-20.3	-208	-4.0	25 psi	STAG
A.Lindbergh	5A-6CW-56-6 W4M	production casing	Clearwater	94/10/04	-64.4		-26.6		-17.1		-20.3		-12.3	100 lbs	STAG
H.	3A-12-48-1 W4M	tubing production	Cummings	94/03/11	-66.2	-284	-30.9	-206	-24.9	-205	-22.5	-271	-8.3		
H.	15A-25-47-11 W4M	tubing production	Cummings	94/03/11	-64.8	-292	-29.9	-216	-22.7	-276	-20.7	-232	-7.8		
A.Lindbergh	11A-22-55-5 W4M	production casing	Cummings	94/03/01	-62.7	-319	-23.5	-209	-19.1	-144	-22.8	-202	-10.8		
A.Lindbergh	11-2-55-6 W4M	production casing	Cummings	94/05/13	-60.4	-302	-20.9	-277	-18.7	-259	-20.6	-272	-12.5	450 psi	
A.Lindbergh	13A-12-55-6 W4M	production casing	Cummings	94/06/12	-49.6	-314	-18.3	-166	-17.5	-178	-26.5	-168	-7.2	10 kPa	
A.Lindbergh	2-20-55-6 W4M	production casing	Cummings	94/06/15	-61.9	-325	-23.4	-177	-17.4	-176	-19.6	-202	-6.7	10 kPa	
A.Lindbergh	3-29-55-6 W4M	production casing	Cummings	94/06/15					-16.1	-228	-19.0	-319	-11.3	10 kPa	*
A.Lindbergh	3-29-55-6 W4M	production casing	Cummings	94/08/19	-55.0	-300		-246	-19.4	-287	-19.8	-264	-1.9		*
A.Lindbergh	10-32-55-6 W4M	production casing	Cummings	94/08/19		-311		-278	-14.3	-275	-23.9	-241	-1.8		*
A.Lindbergh	4A-33-55-6 W4M	production casing	Cummings	94/06/28		-212		-253		-213	-20.3	-227	-12.1		*
A.Lindbergh	9-34-55-6 W4M	production casing	Cummings	94/08/09		-314		-237	-15.2		-19.5	-252	-11.7	10 kPa	*
A.Lindbergh	9-34-55-6 W4M	production casing	Cummings	94/08/19		-263		-192	-16.2	-192	-20.7	-202	-8.8		*
A.Lindbergh	11C-2-56-6 W4M	production casing	Cummings	94/06/12		-229		-221	-16.9	-191	-20.1	-212	-16.6	10 kPa	*
A.Lindbergh	11C-2-56-6 W4M	production casing	Cummings	94/08/19	-59.2	-325		-253	-17.5	-266	-22.1	-246	-8.1		
A.Lindbergh	1-5-56-6 W4M	production casing	Cummings	94/06/13			-17.1		-16.2		-16.6		-12.6	10 kPa	*
A.Lindbergh	10-7-56-6 W4M	production casing	Cummings	94/06/13	-57.7	-306	-16.6	-167	-16.2	-164	-21.9	-223	-2.7	10 kPa	
A.Lindbergh	9A-10-56-6 W4M	production casing	Cummings	94/05/31		-267		-168	-14.0	-191	-19.5	-187	-7.2	10 kPa	*
A.Lindbergh	6A-14-56-6 W4M	production casing	Cummings	94/06/12	-56.7		-21.2		-15.4		-22.1		-2.7	10 kPa	*
A.Lindbergh	6A-14-56-6 W4M	production casing	Cummings	94/08/19	-65.5	-374	-23.2	-169	-18.0	-188	-22.6	-194	-3.5		
E.Elk Point	10-19-56-6 W4M	tubing production	Cummings	94/06/12		-246		-208	-17.5	-179	-23.2	-172		10 kPa	*
A.Lindbergh	10-32-56-6 W4M	production casing	Cummings	94/06/13		-258		-182	-16.1	-44	-19.3	-284	-3.1	10 kPa	
A.St.Paul	3A-12Cu-56-7 W4M	production casing	Cummings	94/02/28	-60.3	-323	-22.6	-212	-20.0	-208	-22.3	-236	-3.7		
A.Lindbergh	9A-34-55-6 W4M	production casing	Dina	94/02/22	-53.6		-22.0	-199	-24.3	-218	-20.5	-178	-8.4		
A.Lindbergh	15-33-55-6 W4M	production casing	Dina	94/03/30	-57.6	-287	-21.6	-189	-24.4	-184	-24.3	-199	-12.0		
H.Wainwright	2C-31-44-4 W4M	tubing production	Nisku	94/01/10	-63.8	-278	-29.3	-192	-21.2	-215	-24.1	-178	-3.3		
H.Wainwright	10C-31-44-4 W4M	tubing production	Camrose	94/01/10	-63.7	-321	-28.9	-182	-23.0	-211	-23.9	-204	-1.9	700 ppm	
H.Wainwright	4-5-45-4 W4M	tubing production	Camrose	94/01/10	-65.8	-311	-28.9	-216		-168	-24.6	-190	-6.4	2800 ppm	

Table A2.2 : $\delta^{13}C$ (PDB) and δD (SMOW) values (‰) of the hydrocarbon components of leaking gas well samples from the Lloydminster region.

Company (Region)	Well	Sample Type	Formation	Date	C1 $\delta^{13}C$	C1 $\delta^{2}H$	C2 $\delta^{13}C$	C2 $\delta^{2}H$	C3 $\delta^{13}C$	C3 $\delta^{2}H$	C4 $\delta^{13}C$	C4 $\delta^{2}H$	CO_2 $\delta^{13}C$	P	Note
H.	6-8-49-6 W4M	"surface casing vent?"		94/07/13	-65.6	-321	-26.1		-19.4	-259	-21.9		-8.4		CAP
H.	11-3-50-4 W4M	surface casing vent		94/05/12	-70.3	-287	-37.9	-125	-24.6	-180	-23.1	-192	-15.2		D&A
A.	3-16-51-9 W4M	surface casing vent		94/08/16	-67.6	-316	-39.9	-200	-22.8	-259	-15.6	-281	-14.5		
A.	3-16-51-9 W4M	surface casing vent		94/08/16	-69.8	-347		-210	-26.6	-191	-23.2	-187	-23.7		
A.Lindbergh	5-16-55-4 W4M	surface casing vent	(Sparky)	94/06/22	-58.2	-302	-17.3	-258	-17.4	-184	-18.1	-181	-13.1		
PCP Lindbergh	6A-17-55-4 W4M	surface casing vent	(Sparky)	94/10/18	-60.3	-320		-221	-19.9	-221	-21.3	-221	-12.7	10 kPa	*
PCP Lindbergh	6A-17-55-4 W4M	surface casing vent	(Sparky)	94/10/18	-67.8	-340	-38.4	-301	-20.7		-22.8	-295	-13.3	10 kPa	
PCP Lindbergh	6A-17-55-4 W4M	production casing	Sparky	94/10/18		-273	-13.1	-322	-16.3	-247	-19.8	-287	-11.7		*
PCP Lindbergh	6A-17-55-4 W4M	production casing	Sparky	94/10/18		-237	-15.4	-157	-18.3	-208	-19.3	-225	-11.8		*
PCP Lindbergh	16A-17-55-4 W4M	surface casing vent		94/10/18	-75.1	-329	-44.1	-164	-23.2	-191	-23.1	-221	-15.8	40 kPa	
PCP Lindbergh	16A-17-55-4 W4M	surface casing vent		94/10/18		-249		-184	-19.7	-293	-23.0	-320	-12.7	10 kPa	*
PCP Lindbergh	16A-17-55-4 W4M	production casing		94/10/18	-68.2	-366	-41.9	-221	-21.4	-245	-22.3	-238	-18.2	40 kPa	*
PCP Lindbergh	16A-17-55-4 W4M	production casing		94/10/18									-12.5	40 kPa	*
A.Lindbergh	1A-20-55-4 W4M	surface casing vent	(Sparky)	94/07/12	-60.2	-302	-33.9	-202	-19.2	-266	-18.1	-208	-13.4		
A.Lindbergh	11A-29-55-4 W4M	surface casing vent	(Sparky)	94/07/13	-72.3	-303	-29.2	-160	-19.5	-227	-18.7	-165	-11.4		
A.Lindbergh	4-9-55-5 W4M	surface casing vent	(Colony)	94/03/01	-62.2	-288	-31.6	-236	-21.2	-197	-22.6	-229	-12.1		
A.Lindbergh	4D2-18-55-5 W4M	surface casing vent (low flow)	(Cummings)	94/05/06	-64.7	-287		-250	-16.6	-224	-18.8	-254			*
A.Lindbergh	4D2-18-55-5 W4M	surface casing vent (low flow)	(Cummings)	94/05/06	-61.2	-294	-28.8	-234	-18.1	-260	-18.4	-249	-14.2		*
A.Lindbergh	4D2-18-55-5 W4M	surface casing vent (flowed into bag)	(Cummings)	94/05/19	-51.6	-281	-34.3		-19.9		-17.1	-220	-14.2	1 kPa	
A.Lindbergh	4D2-18-55-5 W4M	surface casing vent (pumped into bag)	(Cummings)	94/05/18	-67.7	-320	-41.7	-220	-21.4	-182	-18.0		-12.9	0 kPa	
A.Lindbergh	4D2-18-55-5 W4M	surface casing vent	(Cummings)	94/05/31	-64.9	-271	-39.9	-214	-23.4	-198	-18.7	-208		250 kPa	
A.Lindbergh	4D2-18-55-5 W4M	production casing	Cummings	94/05/31		-229	-18.9	-209	-16.3	-280	-20.1		-11.7	20 kPa	*
A.Lindbergh	4D2-18-55-5 W4M	production casing	2nd White Specks	94/12/07	-73.4		-39.8		-19.1		-16.8		-14.6		
A.Lindbergh	4D2-18-55-5 W4M	production casing	2nd White Specks	94/12/07	-58.7		-30.4	-208	-20.9		-22.6		-12.6		
A.Lindbergh	15-18-55-5 W4M	surface casing vent	(Sparky)	94/04/21	-66.6	-297	-39.6	-159	-21.7	-143	-20.9	-187	-14.5		
A.Lindbergh	15-18-55-5 W4M	surface casing vent (20 min start in)	(Sparky)	94/04/21	-65.8	-312	-35.9	-259	-19.7	-165	-18.8	-213	-13.6		
A.Lindbergh	15-18-55-5 W4M	surface casing vent	(Sparky)	94/04/23	-69.6	-317	-42.6	-292	-22.7	-190	-22.3	-188	-26.2		
A.Lindbergh	15-18-55-5 W4M	surface casing vent	(Sparky)	94/04/23	-69.7	-318	-42.8	-284	-21.1		-18.8		-12.3		*
A.Lindbergh	15-18-55-5 W4M	South East corner (bubbles in water)	(Sparky)	94/04/23	-62.3	-208		-227	-15.7	-214	-17.0	-264	-15.4		*
A.Lindbergh	15-18-55-5 W4M	well culvert edge (bubbles in water)	(Sparky)	94/05/19	-66.3	-355	-41.2	-318	-23.0	-240	-17.7	-198	-20.8	0 kPa	+
A.Lindbergh	15-18-55-5 W4M	well culvert edge (bubbles in water)	(Sparky)	94/05/19	-67.1	-344	-40.5	-329	-22.8	-392	-19.2	-264	-15.9	0 kPa	+
A.Lindbergh	8A-24-55-5 W4M	"surface casing vent?"	(Sparky)	94/04/22	-66.5		-32.0	-260	-20.5	-193	-23.7	-171	-16.3		?
A.Lindbergh	16-4-55-6 W4M	surface in well crib	(Sparky)	94/04/20	-69.4	-308	-40.6	-216	-24.0	-194	-22.2	-210	-21.8		
A.Lindbergh	16-4-55-6 W4M	well culvert edge (bubbles in mud)	(Sparky)	94/05/19	-67.1	-337	-44.0	-337	-18.5	-210	-23.1		-20.6	0 kPa	
A.Lindbergh	16-4-55-6 W4M	production casing	"Sparky"	94/04/22	-66.5	-307	-40.2	-164	-22.2	-178	-19.9	-222	-13.2		STAG
A.Lindbergh	16-4-55-6 W4M	production casing	"Sparky"	94/05/10	-60.5	-300	-37.3	-241	-21.8	-261	-21.1	-266	-14.5		STAG
A.Lindbergh	16-4-55-6 W4M	production casing	"Sparky"	94/05/10	-60.8		-38.5			-155	-22.5				STAG
A.Lindbergh	16-4-55-6 W4M	production casing	"Sparky"	94/05/19	-58.4	-301	-37.3	-281	-21.1	-283	-22.5	-283	-17.0	10 psi	
A.Lindbergh	16-4-55-6 W4M	production casing	Sparky	94/12/07	-64.7	-310	-26.2	-220	-19.0	-205	-20.0	-205	-9.1		
A.Lindbergh	16-4-55-6 W4M	production casing	Sparky	94/12/07	-69.5		-24.5			-233	-16.8	-221	-9.2		
A.Lindbergh	16A-4-55-6 W4M	production casing	"Sparky"	94/07/27	-70.1	-323	-41.1	-319		-266	-21.2	-230	-16.5	10 kPa	STAG
A.Lindbergh	1A-5-55-6 W4M	well culvert edge (bubbles in water)	(Cummings)	94/06/13	-67.7	-306	-42.6	-171	-36.2	-294	-32.0	-287	-6.3		
A.Lindbergh	1A-5-55-6 W4M	well culvert edge (bubbles in water)	(Cummings)	94/06/13	-69.4	-310	-38.1	-186	-22.1	-227	-20.8	-301	-14.0		
A.Lindbergh	1-5-55-6 W4M	production casing	Cummings	94/08/19	-62.9	-326	-26.0	-278	-28.0	-182	-21.6	-230	-3.1		
A.Lindbergh	9-6-55-6 W4M	surface casing vent	(Colony)	93/09/08	-68.4	-319	-40.5	-296		-256	-26.8	-236	-8.8		
A.Lindbergh	9-6-55-6 W4M	surface casing vent	(2nd White Specks)	93/10/07	-66.6	-314	-43.7	-183	-22.5	-208	-20.6	-212	-14.9		
A.Lindbergh	9-6-55-6 W4M	surface casing vent	(2nd White Specks)	94/02/04	-67.2	-304	-42.8	-200	-22.6	-171	-23.6	-190	-18.5		
A.Lindbergh	9-6-55-6 W4M	surface casing vent	(2nd White Specks)	94/05/19	-67.1	-194	-42.5	-261	-21.7				-14.1	5 lbs	
A.Lindbergh	9-6-55-6 W4M	surface casing vent	(shallow)	94/07/27	-72.5	-317	-45.2	-199	-24.1	-202	-22.5	-216	-14.3	180 psi	

Company (Region)	Well	Sample Type	Formation	Date	C1 $\delta^{13}C$	C1 $\delta^{2}H$	C2 $\delta^{13}C$	C2 $\delta^{2}H$	C3 $\delta^{13}C$	C3 $\delta^{2}H$	C4 $\delta^{13}C$	C4 $\delta^{2}H$	CO2 $\delta^{13}C$	P	Note
A.Lindbergh	9-6-55-6 W4M	surface casing vent	(shallow)	94/07/27	-69.3	-290		-200	-24.6	-168	-22.6	-174	-10.9	180 psi	
A.Lindbergh	9-6-55-6 W4M	surface casing vent	(shallow)	94/09/11	-73.6	-329	-44.5	-186	-22.4	-204	-21.7	-205	-12.0	10 kPa	
A.Lindbergh	9-6-55-6 W4M	surface casing vent	(shallow)	94/09/11	-72.5	-325		-175	-22.8	-160	-20.5	-167	-3.9	10 kPa	
A.Lindbergh	9-6-55-6 W4M	tubing production	Colony	93/09/08	-59.1	-282	-28.1	-223	-20.4	-179	-21.7	-203	-15.4		
A.Lindbergh	9-6-55-6 W4M	tubing production	2nd White Specks	93/10/07	-67.8	-319	-41.6	-259	-17.8	-244	-22.6	-235	-7.5		
A.Lindbergh	9-6-55-6 W4M	tubing production	2nd White Specks	94/02/22	-68.9		-38.8		-19.6		-20.5		-15.8		
A.Lindbergh	9-6-55-6 W4M	tubing production	2nd White Specks	94/05/19		-314	-37.5	-261	-19.7		-18.5	-193	-12.3	10 lbs	*
A.Lindbergh	9-6-55-6 W4M	tubing production	shallow	94/07/27	-70.5	-318	-44.8	-232	-21.6	-173	-21.8	-231	-11.0	10 kPa	
A.Lindbergh	9-6-55-6 W4M	tubing production	shallow	94/07/27	-69.2	-284	-35.5		-16.7		-18.9		-13.8	10 kPa	
A.Lindbergh	16-8-55-6 W4M	surface casing vent	(2nd White Specks)	95/02/07	-74.7		-45.4				-21.3		-16.4	10 kPa	
A.Lindbergh	16-8-55-6 W4M	tubing production	2nd White Specks	95/02/06	-73.5		-43.6						-20.4	100 kPa	
A.Lindbergh	16-8-55-6 W4M	tubing production	2nd White Specks	95/02/06							-17.5		-16.3	100 kPa	*
A.Lindbergh	16A-8-55-6 W4M	surface casing vent	(2nd White Specks)	94/05/31	-70.5		-44.8		-19.7		-21.3		-13.9	1000 kPa	D&A
A.Lindbergh	16A-8-55-6 W4M	surface casing vent	(2nd White Specks)	94/05/31					-17.0		-20.0		-11.9	1000 kPa	D&A*
A.Lindbergh	14A-26-55-6 W4M	surface casing vent	(Cummings)	94/05/15	-70.0	-311	-32.3	-343	-22.8		-28.2	-349			
A.Lindbergh	1A-3-56-5 W4M	surface casing vent	(Sparky)	94/07/13	-67.0		-36.5		-15.8		-21.0		-17.7		
A.Lindbergh	7A-3-56-5 W4M	surface casing vent	(Cummings)	94/04/20	-55.6	-288		-246	-19.5	-242	-17.8	-227	-11.8		*
A.Lindbergh	7A-3-56-5 W4M	surface casing vent	(Cummings)	94/04/20	-63.4	-307	-32.6	-181	-21.8	-195	-21.7	-275	-15.0		
A.Lindbergh	7-3-56-5 W4M	production casing	Cummings	94/04/22	-59.6	-319	-30.8	-170	-19.1	-212	-21.0	-234	-6.2		

APPENDIX 3

Gas Well Isotope Data of the Kindersley and Medicine Hat Regions

The Kindersley region gas samples were analyzed the same way as the Lloydminster area gases (see Chapter 1.4). The samples from the Medicine Hat region were analyzed in a similar manner, but a cryogenic bath was added to the gas chromatograph. This addition dropped the initial temperature from 40 °C to -75 °C and yielded better separation of the eluent peaks (especially the air and methane peaks).

Company : A. = Amoco Canada Petroleum Company Limited
PCP = PanCanadian Petroleum Limited

These companies often have partners at the listed properties, and the major partner and operator is given.

Region : major oil field well lies in

Well : Legal subdivision - Section - Township - Range

A given well may have several samples of the same date. Those of the same date are not repeat analyses, but rather duplicate samples.

Sample type : tubing production = formation gas sample where the gas came up the inside of the tubing
production casing = formation gas sample where the gas came up outside of the tubing (between the tubing and the casing)

Formation : Table A3.2 has the sampled production horizons arranged by stratigraphic depth. (The stratigraphy of the Medicine Hat region is listed in Table A3.1.)

Date : sampling date

Data : The carbon and hydrogen isotopic data are listed in units of ‰ relative to PDB and SMOW, respectively.

C_1 = methane

C_2 = ethane

C_3 = propane

C_4 = butane

P : source pressure

H_2S : H_2S concentration

Note: ! = dual completed well (the second producing formation is also given)

Table A3.1. Stratigraphic correlation chart of shallow Cretaceous strata of southern Alberta and Saskatchewan (modified after Simpson, 1984).

	SOUTHEAST ALBERTA	SOUTHWEST SASKATCHEWAN
UPPER CRETACEOUS	Oldman	Belly River
	Foremost	
	Pakowki	Lea Park
	Milk River	
	First White Speckled Shale	First White Speckled Shale
		Medicine Hat
	shale	shale
	Second White Speckled Shale	Second White Speckled Shale
	shale	shale
	Fish Scale	Fish Scale

Table A3.2 : $\delta^{13}C$ (PDB) and δD (SMOW) values (‰) of the hydrocarbon components of production gases of the Kindersley and Medicine Hat regions.

Company (Region)	Well	Sample Type	Formation	Date	C1 $\delta^{13}C$	C1 $\delta^{2}D$	C2 $\delta^{13}C$	C2 $\delta^{2}H$	C3 $\delta^{13}C$	C3 $\delta^{2}H$	C4 $\delta^{13}C$	C4 $\delta^{2}H$	CO_2 $\delta^{13}C$	P / H2S	Note
A.	10-6-31-26 W3M	tubing production	Bakken	94/12/19	-69.2	-379	-29.1	-213	-26.9	-294	-25.7	-222	-18.4	925 psi	
A.	4-7-31-26 W3M	production casing	Bakken	94/12/19	-69.4	-300	-30.4	-151	-24.2	-268		-176	-21.3	30 psi	
A.	5-7-31-26 W3M	production casing	Bakken	94/12/19	-70.3	-310	-33.6	-194	-29.9	-202	-29.5	-203		30 psi	
PCP Cassils SG	14-24-19-15 W4M	tubing production	Milk River	94/08/09	-70.2	-318	-45.9	-210	-13.7		-20.6		-19.5	1130 kPa; 0 ppm	I Medicine Hat
PCP Cassils SG	14-24-19-15 W4M	tubing production	Milk River	94/08/09	-70.5	-314	-44.7	-227	-12.6		-15.2	-179	-20.8	1130 kPa; 0 ppm	I Medicine Hat
PCP Cassils SG	14-24-19-15 W4M	tubing production	Medicine Hat	94/08/09	-71.4	-308	-42.9	-195	-13.8	-198	-17.2	-170	-16.8	1130 kPa; 0 ppm	I Milk River
PCP Cassils SG	14-24-19-15 W4M	tubing production	Medicine Hat	94/08/09	-70.6	-259	-47.9	-229	-11.5	-186	-20.6	-129	-18.7	1130 kPa; 0 ppm	I Milk River
PCP Cassils SG	14-27-19-15 W4M	tubing production	2nd White Specks	94/08/09	-69.6		-46.8		-10.7		-27.9		-29.4	1122 kPa; 0 ppm	
PCP Cassils SG	14-27-19-15 W4M	tubing production	2nd White Specks	94/08/09	-69.1	-331	-44.9	-228	-11.3		-18.2		-25.2	1122 kPa; 0 ppm	

APPENDIX 4

Water Analyses in the Lloydminster Area

4.1 Introduction

Natural gas migrating toward surface along or near well casings may also diffuse laterally. Plumes of aqueous methane could spread via advective-dispersion transport relatively quickly into aquifers cut by production wells. The hydrocarbons may also migrate laterally as a gas phase (bubble) through the groundwater reservoirs (Saskatchewan Research Council, 1995).

Along with the migration of hydrocarbons from reservoirs located in deeper strata, natural gas in the groundwaters may be a product of bacterial methanogenesis. The contribution of such in-situ processes in the Lloydminster region is not known (Wassenaar and Lollar, 1994; Saskatchewan Research Council, 1995). Resolution of the relative contribution of these two components using isotopic analyses of methane or gas chemistry (C_1:C_{2+} ratios) is restricted as the gas of the Lloydminster area reservoirs appear to be primarily of bacteriogenic origin.

4.2 Sampling Sites and Methods

Monitoring well samples were obtained from two sites in the vicinity of Lloydminster. One study site was in the Lindbergh region; the other was located in Saskatchewan's Aberfeldy field.

The five monitoring wells of the Lindbergh site (~ 30 m deep) surround a "leaking" Amoco Canada Petroleum gas well (16-4-55-6 W4M) which produced from the Cummings and Sparky Formations between 1983 and 1987 (Figure A4.1). The five Aberfeldy monitoring wells (~ 20 m deep) surround a "leaking" Husky Oil production well (C14-16-49-26 W3M) (Figure A4.2). The production well at this locale, informally

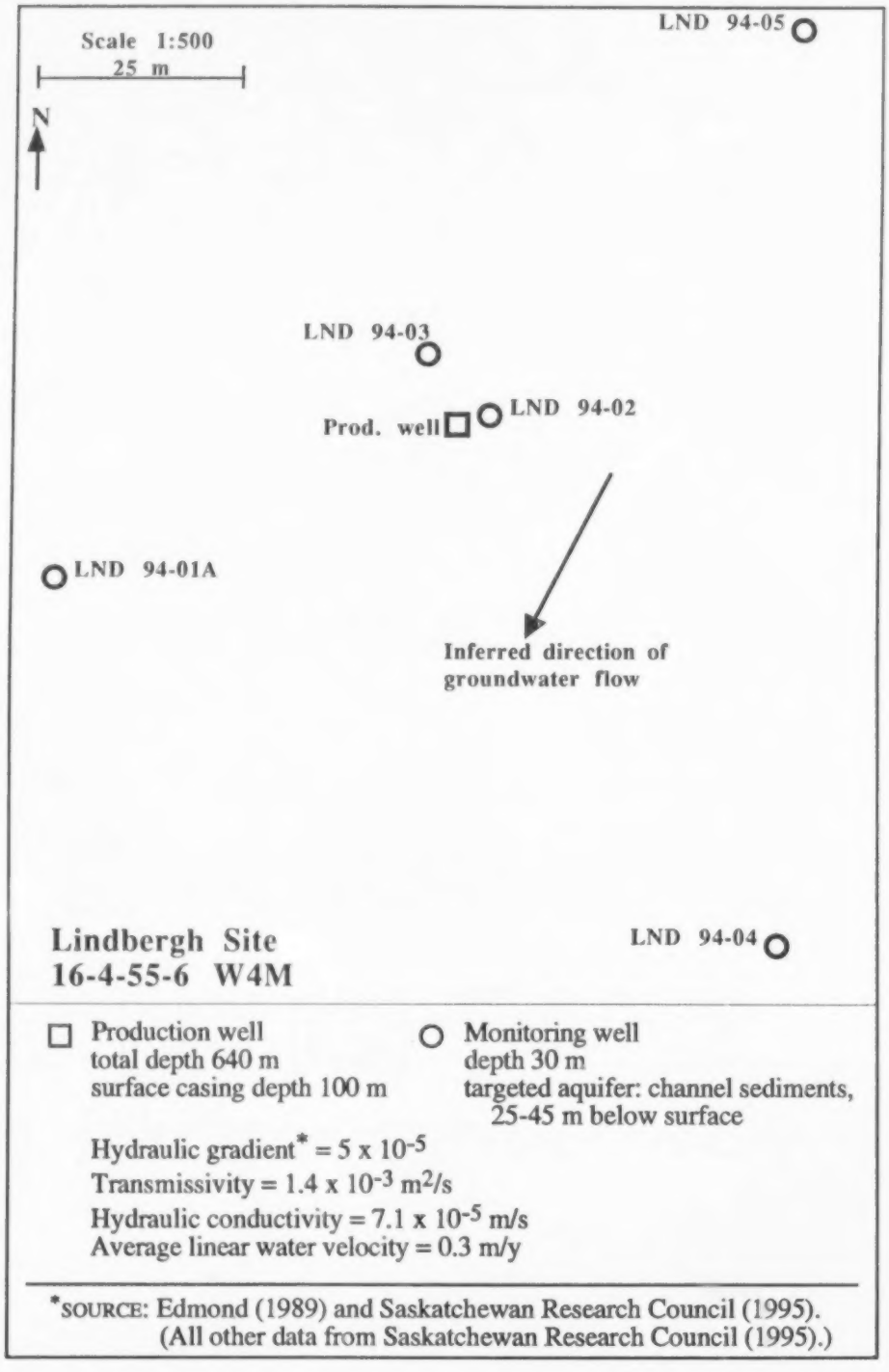

Figure A4.1. Map of the Lindbergh site wells and hydrogeological data (modified after Saskatchewan Research Council, 1995).

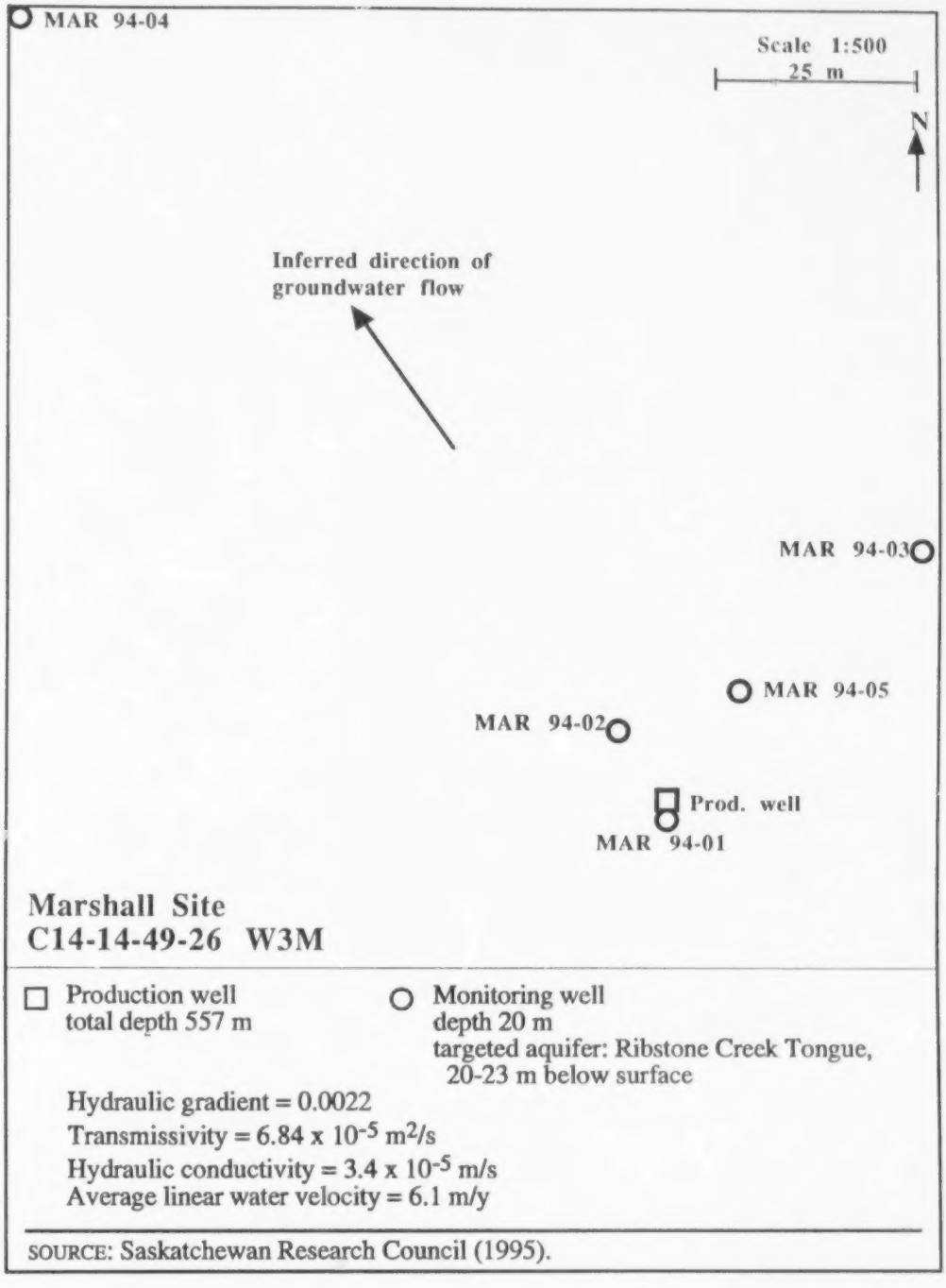

Figure A4.2. Map of the Marshall site wells and hydrogeological data (modified after Saskatchewan Research Council, 1995).

referred to as the "Marshall site," was completed in 1965 and produced from the Sparky Formation. The oil wells at both sites are no longer in production. Gas bubbles have been observed coming up through the mud and water pools surrounding the producing wellhead at the Lindbergh site, and very high natural gas concentrations have been detected in soil pores up to 3 m from the Marshall site wellhead (Saskatchewan Research Council, 1995). These two sites were chosen for research because of this obvious gas leakage and because of their relative isolation from other production wells and the presence of shallow (< 50 m) aquifers in the vicinity (Millard, 1990; Ozoray *et al.*, 1994).

The major dissolved ion (Ca^{2+}, Mg^{2+}, K^+, Na^+, Cl^-, HCO_3^- and SO_4^{2-}), nutrient (nitrate and nitrite) and trace metal (Fe and Mn) content and physical properties (pH and Eh) of the water samples were determined by the Saskatchewan Research Council (1995). The samples were also analyzed for their deuterium (D) fraction and the ^{13}C content of their dissolved inorganic carbon (DIC) content. The D content of the waters was obtained by heating them with Zn metal (Coleman *et al.*, 1982) and isotopically analyzing the produced H_2 gas. The DIC fraction of the water (aqueous CO_2, H_2CO_3, HCO_3^- and CO_3^{2-}) was collected as $CO_{2(g)}$ by reacting the water with concentrated phosphoric acid. The H_2 and CO_2 were analyzed on a Finnigan-MAT 252. The isotope data are reported in the usual δ notation, with SMOW as the standard for D (Hagemann *et al.*, 1970) and PDB as the ^{13}C standard (Craig, 1957).

4.3 Results and Discussion

The groundwater chemistry and isotope data are summarized in Tables A4.1 and A4.2 . The D content of the Lindbergh site aquifer is low ($\delta D_{(SMOW)} \approx -155$ ‰). The D/H ratio of this near-surface water discharge zone (Edmond, 1989) is significantly lower than that of the deeper formation water (δD Cummings $_{(SMOW)} \approx -105$ ‰).

The methane concentration of the groundwater is highest in those wells closest to the production wells (LND 94-02 and MAR 94-01). At the Lindbergh site, the high

Table A4.1. Groundwater chemistry* and isotopic composition of the Lindbergh site monitoring wells.

Analyte	Units	LND 94-01A	LND 94-02	LND 94-03	LND 94-04	LND 94-05
Methane	µg/mL	0.05	8.59	0.02	0.03	0.01
Ethane	µg/mL	ND	0.05	ND	ND	ND
Ca^{2+}	mg/L	156	158	147	154	147
Mg^{2+}	mg/L	58	57	61	61	59
K^{+}	mg/L	6.2	5.4	5.9	6.8	4.9
Na^{+}	mg/L	128	115	121	101	90
Cl^{-}	mg/L	20	20	19	18	18
HCO_3^{-}	mg/L	562	572	582	574	548
SO_4^{2-}	mg/L	393	379	390	381	345
NO_3^{-}/NO_2^{-}	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
Fe^{2+}/Fe^{3+}	mg/L	2.8	5.4	4.2	1.2	0.7
Mn^{2+}	mg/L	0.9	2.1	1.5	0.7	0.3
$\sum$ Ions	mg/L	1323	1308	1327	1297	1213
pH		6.66	7.02	6.95	6.90	6.99
Eh	mV	31.7	11.9	15.1	-34.2	-44.1
δ D (H_2O)	‰ SMOW	-151	-156	-160		
$\delta^{13}C$ (DIC)	‰ PDB	-14.0	-15.7	-14.5	-15.0	-14.2

* SOURCE: Saskatchewan Research Council (1995)
ND: not detectable

Table A4.2. Groundwater chemistry* and isotopic composition of the Marshall site monitoring wells.

Analyte	Units	MAR 94-01	MAR 94-02	MAR 94-03	MAR 94-04	MAR 94-05
Methane	µg/mL	0.10	0.02	0.003	0.04	0.01
Ethane	µg/mL	ND	ND	ND	ND	ND
Ca^{2+}	mg/L	127	142	205	169	168
Mg^{2+}	mg/L	48	51	76	62	63
K^{+}	mg/L	6.4	5.9	6.4	6.8	6.6
Na^{+}	mg/L	99	42	63	55	58
Cl^{-}	mg/L	4	2	3	4	4
HCO_3^{-}	mg/L	525	571	618	579	568
SO_4^{2-}	mg/L	276	204	427	283	309
NO_3^{-}/NO_2^{-}	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01
Fe^{2+}/Fe^{3+}	mg/L	1.4	1.3	2.7	0.5	0.9
Mn^{2+}	mg/L	0.2	0.3	0.2	0.7	0.4
Σ Ions	mg/L	1084	1018	1399	1158	1176
pH		7.28	7.18	6.98	7.01	7.17
Eh	mV	-38.4	-32.6	-22.4	-39.9	-45.6
$\delta^{13}C$ (DIC)	‰ PDB		-12.6			-13.4

* SOURCE: Saskatchewan Research Council (1995)
ND = not detectable

methane concentration detected in the nearest monitoring well was accompanied by measurable ethane and suggests the presence of a natural gas plume in the aquifer caused by leakage associated with the production well. The methane concentration found in the water of the other wells in this region was low. Perhaps these values are a reflection of the background methane concentration of the aquifer. The methane concentration in the Marshall site monitoring wells decreased with distance from the production well, with the exception of the farthest well (MAR 94-04) which had a higher methane concentration than all wells but the closest (MAR 94-01). The MAR 94-04 well is located ~ 130 m downgradient of the Husky Oil production well, and its methane concentration may be indicative of its lying in the center of the plume. The other four monitoring wells would be situated outside the plume, and the methane content of MAR 94-03 (the farthest of these four) waters may be the natural background level in the Ribstone Creek member aquifer in this region. At both sites, a low methane concentration is a probable intrinsic characteristic of the aquifers. The gas may be diffusing from the underlying Colorado Group shales present in both locales (Drimmie *et al.*, 1991). Even the highest methane concentrations detected are at least one order of magnitude lower than the inferred saturated dissolved concentrations for the Lindbergh and Marshall site aquifers (112 mg/L and 74 mg/L, respectively) (Saskatchewan Research Council, 1995). Thus, these two natural gas plumes are not considered large environmental risks.

The Saskatchewan Research Council's (1995) attempts at modeling the methane plume of the Marshall site using the PATCH3D analytical model (Sudicky *et al.*, 1988) were unsuccessful when only advection-dispersion and sorption processes were included. A reasonable simulation of the observed data was established when an exponential decline of the methane source concentration was incorporated into the model. This implies that either the methane flux from the deep gas migration source has dropped notably over time (depletion of reservoirs near the source) or the rate of gas biodegradation near the production well has been increasing over time. In either case, the

data suggest that the methane concentration at or near the plume source has been falling over time.

In neither site is there evidence that "leakage" from the production wells is affecting dissolved ions. (The chloride concentration remains relatively constant throughout the two leases.)

The sum of the dissolved ions is relatively constant at the Lindbergh site, but varies between 1084 and 1399 mg/L at the Aberfeldy locale. This change in total dissolved ion concentration is a reflection of varying sulphate concentration. The sulphate concentration decreases in the vicinity of the of the Husky Oil production well and is greatest at the locale of MAR 94-03. The opposing changes in sulphate and methane concentrations at the Marshall site hint at the simultaneous reduction of sulphate and methane oxidation. Sulphate reduction is a reaction where bacteria use oxygen in SO_4^{2-} to oxidize organic matter (in this case methane) to CO_2, producing sulfides as a by-product (Krouse, 1980; Drever, 1988):

$$SO_4^{2-} + CH_4 \Rightarrow HS^- + HCO_3^- + H_2O, \text{ and}$$

$$HCO3^- + H^+ \Rightarrow CO_2 + H_2O.$$

The notable Fe and Mn concentration, insignificant nitrate/nitrite content and the measured Eh values are indicative of reducing environments at both study sites. Such conditions, along with the trend of increasing bicarbonate concentration with distance from the well, support the reduction of sulphate at the Marshall site. The produced sulfide likely precipitates out of solution as an iron sulfide:

$$HS^- + Fe^{2+} \Rightarrow FeS_{2(s)} + H^+.$$

At the Lindbergh site, there is no notable SO_4^{2-} (or HCO_3^-) concentration trend.

Sulphate reduction as well as bacterial production of methane add organic carbon to the DIC pool (Drimmie *et al.*, 1991). Microbes preferentially utilize ^{12}C, and bacterial methanogenesis either releases ^{13}C-enriched CO_2 as a respiration product ($^*CH_3COOH \Rightarrow {}^*CH_4 + CO_2$) or , if CO_2 reduction is the mechanism ($CO_2 + 4H_2 \Rightarrow CH_4 + 2H_2O$), the residual DIC will be enriched in ^{13}C (Coleman *et al.*, 1981; Balabane *et al.*, 1987; Grossman *et al.*, 1989; Drimmie *et al.*, 1991). In either case, the DIC would be isotopically heavy ($\delta^{13}C$ values close to or ≥ 0 ‰). In contrast, isotopically light DIC results from methane oxidation (Krouse, 1980; Drimmie *et al.*, 1991; Wassenaar and Lollar, 1994). (Microbial oxidation of methane enriches the residual methane in ^{13}C and produces ^{13}C-depleted CO_2.) The observed DIC $\delta^{13}C$ values are low, ranging from -12.6 to -15.7 ‰. The $\delta^{13}C$ value of the DIC is lower in monitoring wells near the production wells. This reinforces the argument of methane oxidation occurring near the gas wells suggested by water chemistry, but as the change in δ values is small, there would be little, if any, oxidation taking place.

4.4 Summary

Gas leakage from oil producing horizons is suspected to be the cause of methane plumes observed within the soil around many wells in the Lloydminster region. These methane plumes extend several meters from the wellbore and often induce damage to crops (Godwin *et al.*, 1990; Jocksch *et al.*, 1993).

Investigations of groundwater chemistry at the Lindbergh and Aberfeldy sites show gas leakage from oil and gas wells to increase the natural gas content of groundwater. Methane analyses, however, indicate that the gas plumes generated by leakage are not of hazardous concentration ($[C_1] < 8.6$ mg/L). Coupled sulphate reduction - methane oxidation reactions appear to exert control over the occurrence of hydrocarbons in the two groundwater systems studied.

Research into the effects of gas migration on groundwater is preliminary.

Continued evaluation of water chemistry is necessary to develop a further understanding of the transport of hydrocarbons in aquifers and the environmental impact of oil and gas industry operations on groundwater systems.